

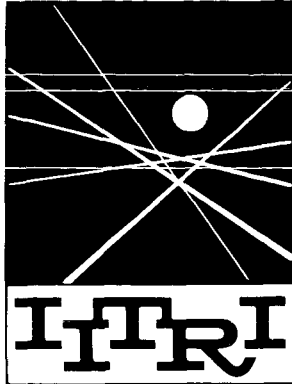
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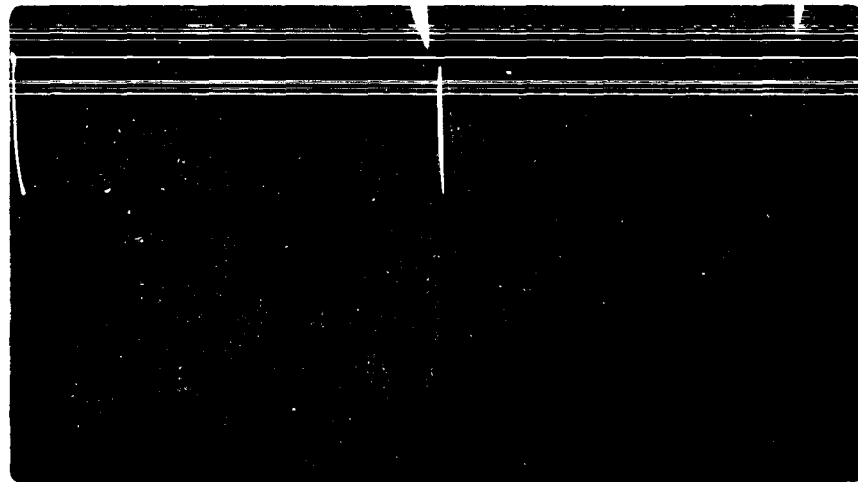
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(Summary Report)

PROTECTIVE COATINGS
FOR REFRACTORY METALS
IN ROCKET ENGINES

National Aeronautics and Space Administration
Washington 25, D. C.

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IIT RESEARCH INSTITUTE
Technology Center
Chicago, Illinois

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ABSTRACT

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This program is directed toward the development of protective coatings for use on tungsten in low pressure radiation-cooled rocket engines at temperatures above 3600°F.

Primary emphasis has been on the investigation of refractory inorganic compounds and composite oxide-refractory metal coating systems. Nitride and carbide coatings were pyrolytically deposited. The composite oxide-metal coatings were produced by plasma spraying and by wet slurry application techniques. In addition, improved silicide coatings and other metal-intermetallic compound systems have been investigated for potential usefulness above 3600°F.

The most promising systems, based on high temperature stability in an oxidizing environment, are composite coatings consisting of layers of $\text{HfO}_2\text{-Y}_2\text{O}_3$ or SrZrO_3 with tungsten produced by plasma spraying.

Author

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PROTECTIVE COATINGS
FOR REFRACTORY METALS
IN ROCKET ENGINES

I. INTRODUCTION

This is a summary report on IITRI Project B237, "Protective Coatings for Refractory Metals in Rocket Engines," covering the period March 9, 1962, to March 8, 1963. The purpose of this program is to develop and evaluate protective coating systems for use on refractory metals in low-pressure, liquid-fueled rocket engines at temperatures above 3600°F. The refractory metals of primary interest are tungsten and tantalum-tungsten alloys. The coating systems which are being investigated are intended for use on the refractory metals as components of radiation-cooled structures.

II. BACKGROUND AND EXPERIMENTAL APPROACH

The use of refractory metals in uncooled, liquid-propellant, rocket engines is severely restricted by the lack of oxidation resistance inherent in these materials and by the accompanying lack of high temperature protective coating systems. This problem is not new; in the past designers of jet, ram-jet, and pure thrust engines have considered the use of various materials to overcome the problems encountered in the severe environment of the engine. The first major effort to protect refractory metals from oxidation was directed toward molybdenum for use in aircraft gas turbines. At the present time, the protection of turbine buckets in jet engines--although it remains unsolved--apparently has been relegated to a position of secondary importance relative to space-vehicle applications.

Relatively thin coatings, primarily silicides, have been developed for all of the refractory metals and can withstand the low thrust developed in small rocket engines at temperatures up to, at most, 3450°F. In addition, refractory metal thrust chambers, nose cones, or leading edge sections have been coated with relatively thick reinforced or graded oxide coatings to withstand temperatures to 4200°F. In addition to coated metals, oxides, and other inorganic compound bodies, intermetallic compounds, cermets, and various composite materials have been investigated for use as components in rocket engines.

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In the past, rocket engine operation under conditions where erosion or loss of material through oxidation can not be tolerated has called for severe restrictions on flame temperature and chamber pressure or has necessitated the design of cooling systems to maintain metal surface temperatures below allowable limits. This program has therefore been initiated with the objective of investigating oxidation-protective coating systems for use on refractory metals at temperatures above 3600°F to allow greater freedom in the design of rocket motors or to permit the use of high-efficiency radiation-cooled engines under conditions where other cooling methods may not be feasible or attractive. The experimental approach in this program includes investigation of refractory materials including oxides, nitrides, carbides, and a variety of composites applied as coatings to refractory metals by the most acceptable methods. Because of the high temperatures of interest, this effort is restricted to only the very high melting refractory materials, tungsten and Ta-10W alloy.

III. EXPERIMENTAL STUDIES

A. Pyrolytic Coatings

1. Introduction

The objective of this approach is to produce fully dense pyrolytic coatings of refractory nitrides and carbides on tungsten and Ta-10W alloy. The inorganic compounds to serve as coatings were selected on the basis of melting point, known or anticipated oxidation resistance, and lack of reactivity with the base metals. In the absence of knowledge of oxidation behavior at very high temperatures, compound selection was based on the probability of the compound forming a high-melting oxide during oxidation.

The compounds which fulfill these requirements most satisfactorily and are adaptable to pyrolytic plating are the nitrides and carbides of the Group IV transition metals, zirconium and hafnium. The melting points of these carbides and of the derived oxides are as follows:

<u>Compound</u>	<u>Melting Point, °F</u>
ZrC	6386
ZrN	5396
ZrO ₂	4910
HfC	7010
HfN	5990
HfO ₂	5252

The oxidation behavior of pyrolytic ZrC and HfC has recently been evaluated in a water-stabilized plasma flame.⁽¹⁾ At 4250°F, both materials were found to oxidize at a rate of 0.1 mils/sec in a 10% H₂O environment. A protective oxide was formed on the carbides during oxidation. In other studies, these carbides were found to be considerably more oxidation resistant than other carbides in a CO₂ atmosphere at temperatures in the 4200°F range. Tests were performed on a variety of materials in an oxygen-hydrogen rocket motor at a flame temperature of 4530°F.⁽²⁾ Of the materials evaluated, ZrC-coated graphite displayed the best oxidation and erosion resistance. The ZrC coatings were found to increase in thickness due to the formation of an adherent ZrO₂ layer.

There is no published information on the oxidation behavior of nitrides, at temperatures above 3600°F, although it may be anticipated that the nitrides of hafnium and zirconium should be as oxidation resistant as the carbides. Wakelyn⁽³⁾ has found that pyrolytic TiN is an effective oxidizable coating for protecting graphite at 3100°F, a temperature which is below the melting point of TiO₂ (3180°F).

The usefulness of these inorganic compounds to serve as protective coatings depends on their lack of interaction with the substrate. Interaction studies between tungsten and inorganic compounds have been performed. Similar studies have not generally been made for tantalum and tantalum-tungsten alloys.

The nitrides of hafnium and zirconium do not interact with tungsten below 5070°F.⁽⁴⁾ This has been substantiated by Singleton⁽⁵⁾ who used HfN as a diffusion barrier between tungsten and graphite at 5500°F. Hafnium carbide reacts with tungsten at 2800°F with the formation of a eutectic. A similar reaction is reported between tungsten and ZrC at a temperature below 4890°F.

Based on existing information, therefore, it appears that for use at temperatures above 3600°F the most promising pyrolytically deposited coating materials appear to be the nitrides of hafnium or zirconium. The carbides of these metals, although apparently oxidation resistant, react with tungsten at relatively low temperatures. Accordingly, the protective capability of nitride coatings was investigated extensively. In addition, some

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effort was expended in an attempt to coat both tungsten and Ta-10W with HfC. This proved unsuccessful and was abandoned.

2. Experimental Procedure

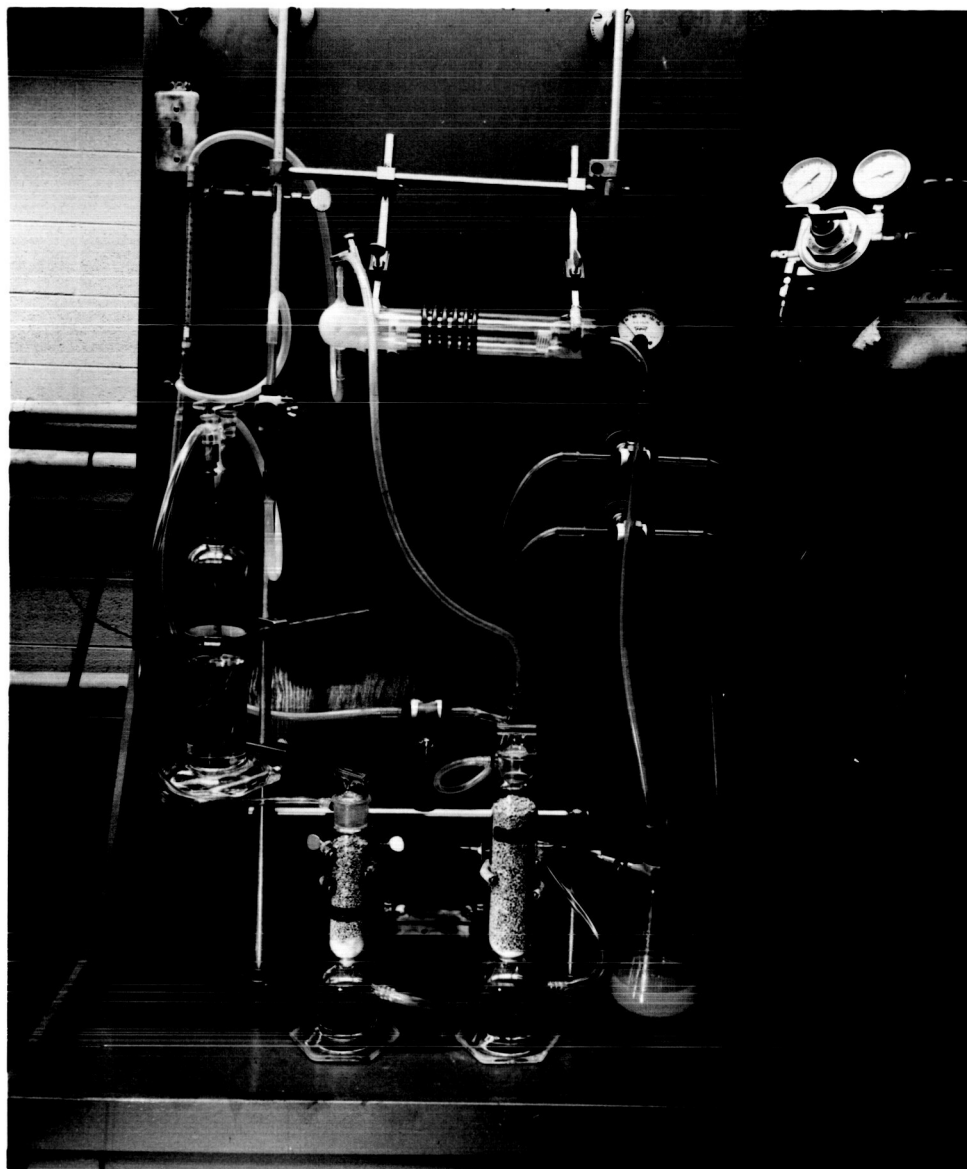
Initially, titanium nitride coatings were deposited onto tungsten rods which were heated inductively. This work was performed primarily to establish plating conditions and to evaluate testing procedures. The apparatus is shown in Figure 1. The procedure used for plating TiN consists of passing a TiCl_4 -saturated, 90v/o nitrogen 10v/o hydrogen gas mixture over the heated tungsten rod. A variation of this procedure was used by Wakelyn⁽³⁾ to coat graphite with TiN, and similar procedures are described by Powell.⁽⁶⁾

A total of 21 TiN-coated specimens were prepared. Plating data appear in Table I. The coatings were applied at temperatures between 2730° and 3250°F for 1 to 20 minutes. Coating thickness increases with time and appears to display a similar temperature dependence. No relationship was established between gas flow rate and coating thickness.

The apparatus in Figure 1 was modified slightly to accommodate solid HfCl_5 for the deposition of HfN. The tetrachloride was sublimed, mixed with nitrogen and hydrogen, and passed over an inductively heated tungsten rod. Plating data appear in Table II. The deposition rate was found to be strongly temperature dependent. At 3630°F, coatings which varied in thickness between 2.6 and 5.0 mils were obtained after 20 minutes. These coatings, which were applied to 0.156 inch diameter rods, weighed from 1.044 to 1.892 grams. The coatings were reasonably uniform along the length of the specimens; however, microexamination revealed radial cracks, some of which extended to the substrate. These cracks are believed to be attributable to differences in thermal expansion of the coating and substrate.

A similar procedure was used to deposit HfN on Ta-10W alloy, after initially depositing a tungsten diffusion barrier. The tungsten was deposited from WCl_6 . Plating data appear in Table III.

In view of their extensive prior experience with pyrolytic carbide deposition, High Temperature Materials, Inc. were asked to apply the ZrC coatings on tungsten and Ta-10W. Unfortunately, however, it was not possible to coat these materials with an adherent layer of hafnium carbide. The



Neg. No. 23298

Figure 1
Vapor plating apparatus

TABLE I
PLATING DATA FOR TiN COATINGS ON TUNGSTEN

Specimen No.	Plating Temperature, °F	Plating Time, min	Gas Flow Rate cc/min	Coating Thickness mils	Coating Weight, grams
1T	2730	1	1200	0.1	--
2T	2730	2	1200	0.5	--
3T	2730	2	1200	0.2	--
4T	2730	2	800	0.2	--
5T	2730	2	800	0.2	--
6T	2730	10	800	0.8	--
7T	2730	20	800	1.5	--
8T	2730	10	800	0.8	--
9T	2900	20	1200	2.5	0.5
10T	2900	2	1200	0.2	0.1
11T	2900	2	1200	0.2	0.1
12T	2900	2	1200	--	--
13T	2900	20	1200	2.6	0.5
14T	2900	20	1200	2.5	0.6
15T	2900	2	800	0.2	--
16T	2900	20	800	2.5	0.5
17T	2900	20	800	2.5	0.5
18T	2900	10	800	1.0	0.3
19T	3250	20	1200	4.0	0.5
20T	3250	20	1200	4.0	0.5
21T	3250	20	1200	2.5	0.5

TABLE II
PLATING DATA FOR HfN COATINGS ON TUNGSTEN

Specimen No.	Plating Temperature °F	Plating Time, min	Gas Flow Rate cc/min	Coating Thickness mls	Coating Weight, grams
1H	3360	5	1200	0.3	--
2H	3270	20	400	0.5	--
3H	3270	30	600	0.8	0.5
4H	3630	10	800	1.8	0.570
5H	3630	20	800	2.8	1.044
6H	3630	20	800	3.2	1.325
7H	3630	20	1000	3.9	1.504
8H	3630	20	800	5.0	1.892
9H	3630	20	800	3.3	1.291
10H	3630	20	800	4.1	1.697
11H	3630	20	800	3.5	1.440
12H	3630	16	800	2.0	0.836
13H	3630	16	800	3.0	1.061
14H	3630	16	800	2.4	0.985
15H	3630	16	800	3.2	1.480
16H	3630	16	800	3.9	1.549
17H	3630	20	800	2.6	1.159
18H	3630	20	800	--	---

TABLE III

PLATING DATA FOR COATINGS ON Ta-10W ALLOY

Specimen No. *	Plating Temperature °F	Plating Time, min.	Coating(s) Deposited	Coating Thickness, mls	Coating Weight, grams
1TA	3540	10	HfN	---	0.4547
2TA	3630	20	Hf	0.6	0.1202
3TA	3630	20	Hf	0.50	0.0343
4TA	3630	30	Hf	0.08	0.2196
	3630	10	N ₂	---	-----
5TA	3630	25	W	9.7	3.1446
	3630	20	HfN	2.1	1.6555
6TA	3630	10	W	4.2	0.8740
	3630	20	HfN	4.0	1.7437
7TA	3630	5	W	2.1	0.3869
	3630	12	HfN	1.5	0.5785
8TA	3630	10	W	3.5	0.8004
	3630	10	HfN	1.5	0.9636
9TA	3180	15	W	6.3	2.4092
	3630	10	HfN	3.2	1.4287
10TA	3180	10	W	5.0	2.0456
	3630	12	HfN	2.2	1.1021
11TA	3180	10	W	5.0	1.8852
	3630	20	HfN	3.6	1.7578
12TA	3180	10	W	3.9	1.5464
	3630	10	HfN	2.7	1.3674

*Gas flow rate, 800 cc/min in every specimen.

following is a quotation from Dr. R. B. Bourdeau of High Temperature Materials, Inc., describing the reasons for the lack of coating adherence.

"We realized that a thermal expansion difference exists between tungsten ($4.5 \times 10^{-6}/^{\circ}\text{C}$) and HfC ($6.6 \times 10^{-6}/^{\circ}\text{C}$), and that the stresses built up during cooling from process temperatures (1800° - 2000°C) could only be relieved by yielding, cracking, or spalling of the coating. With coatings greater than 0.5 mils the coatings cracked and spalled.

"With tantalum or its alloy which has a higher coefficient (6.5×10^{-6} per $^{\circ}\text{C}$) the chances for success appeared good, but in this case the formation of Ta_2C (probable) at the interface, which was visible by its yellowish color, destroyed the adhesion of the coating. This is not an unusual case, as we have observed this with TAC on graphite and other carbide coatings on tantalum. Ta_2C on graphite has a hexagonal structure while TaC and HfC have cubic structures and the lattice mismatch as well as the thermal contraction mismatch can destroy coating adhesion. With tungsten the formation at the interface of W_2C or WC, which have hexagonal structures with high thermal expansion anisotropies, could be responsible. For example, the coefficients of W_2C are 9.3 and $13 \times 10^{-6}/^{\circ}\text{C}$ and those of WC are 2.1 and $20.5 \times 10^{-6}/^{\circ}\text{C}$.

"These samples are the first tungsten which we have attempted to coat with a carbide and the first Ta attempted with HfC. In view of the results obtained both here and at other laboratories on the coating of tantalum with other carbides, it appears that some barrier coating is required to improve the adhesion of HfC."

3. Experimental Studies

a. Thermal Stability

Initially, thermal stability tests were performed on the nitride coated rods to determine the extent of chemical and physical interaction between the coating and substrate in the absence of an oxidizing environment.

Titanium nitride coatings, as deposited, are relatively crack-free and well bonded to tungsten. Rapid heating to 3630°F at rates of $360^{\circ}\text{F}/\text{min}$ and $200^{\circ}\text{F}/\text{min}$ causes no gross cracking or loss of adherence. Heating at 3630°F for 5 minutes in argon at a pressure of 1 atmosphere, causes a slight discoloration of the nitride although no detectable weight change is observed. The discoloration may be due to impurities in the inert gas.

Hafnium nitride, as previously mentioned, contains radial cracks when deposited on tungsten rods. This may be seen in Figure 2. Rapid



Neg. No. 24533

X250

Figure 2

As-deposited hafnium nitride coating on tungsten.

heating to 3630°F causes an increase in the number and size of cracks.

The coating is unstable in vacuum (10^{-4} torr) at 4120°F. A specimen heated under these conditions underwent a weight loss of 3.50% of the initial coating weight, accompanied by melting. Since nitrogen comprises 7.84% of the weight of stoichiometric HfN, this weight loss can be considered particularly significant if the bulk of the loss is attributable to nitrogen. X-ray diffraction analysis of the surface of the nitride coating after vacuum exposure indicates the presence of α -Hf, W_2 Hf, and apparently nitrogen-deficient HfN. Heating the nitride for five minutes in vacuum at 2820°F causes no dissociation. Similarly, heating in nitrogen at 4100°F at a pressure of 150 mm causes no significant change in the nitride or interaction with the tungsten. Heating at 5000°F under these conditions causes the nitride to lose weight at a slow rate. The change in weight as a function of time is plotted in Figure 3. After 5 min at 5000°F in nitrogen a two-phase structure, apparently nitrogen-saturated α -Hf and nitrogen-deficient HfN, is formed. The hafnium subsequently appears to react with the tungsten to form a W_2 Hf layer between the nitride and base metal. This type of structure may be seen in Figure 4. The two-phase structure that is developed by heating in nitrogen appears to be more crack-free than the as-deposited nitride. Furthermore, it appears that heating at high temperatures in nitrogen can be used to produce a wide variety of mixed nitride-metal coatings. This could prove to be an effective means for controlling thermal expansion behavior.

b. Oxidation Studies

Oxidation tests were performed in static air on TiN-coated tungsten at 3630° and 3090°F. At the lower temperature a protective oxide forms; the rate of oxidation is $+22 \text{ mg/cm}^2/\text{min}$ during the early stages. This corresponds to a surface recession rate of about 0.5 mils/min. Bare tungsten oxidized under identical conditions loses weight at the rate of $110 \text{ mg/cm}^2/\text{min}$. The oxide formed on the nitride appears glazed.

At 3630°F, oxidation of the nitride-coated samples proceeds far more rapidly and specimens lose weight at a rate of $122 \text{ mg/cm}^2/\text{min}$. The rate of weight loss for bare tungsten under these conditions is $360 \text{ mg/cm}^2/\text{min}$.

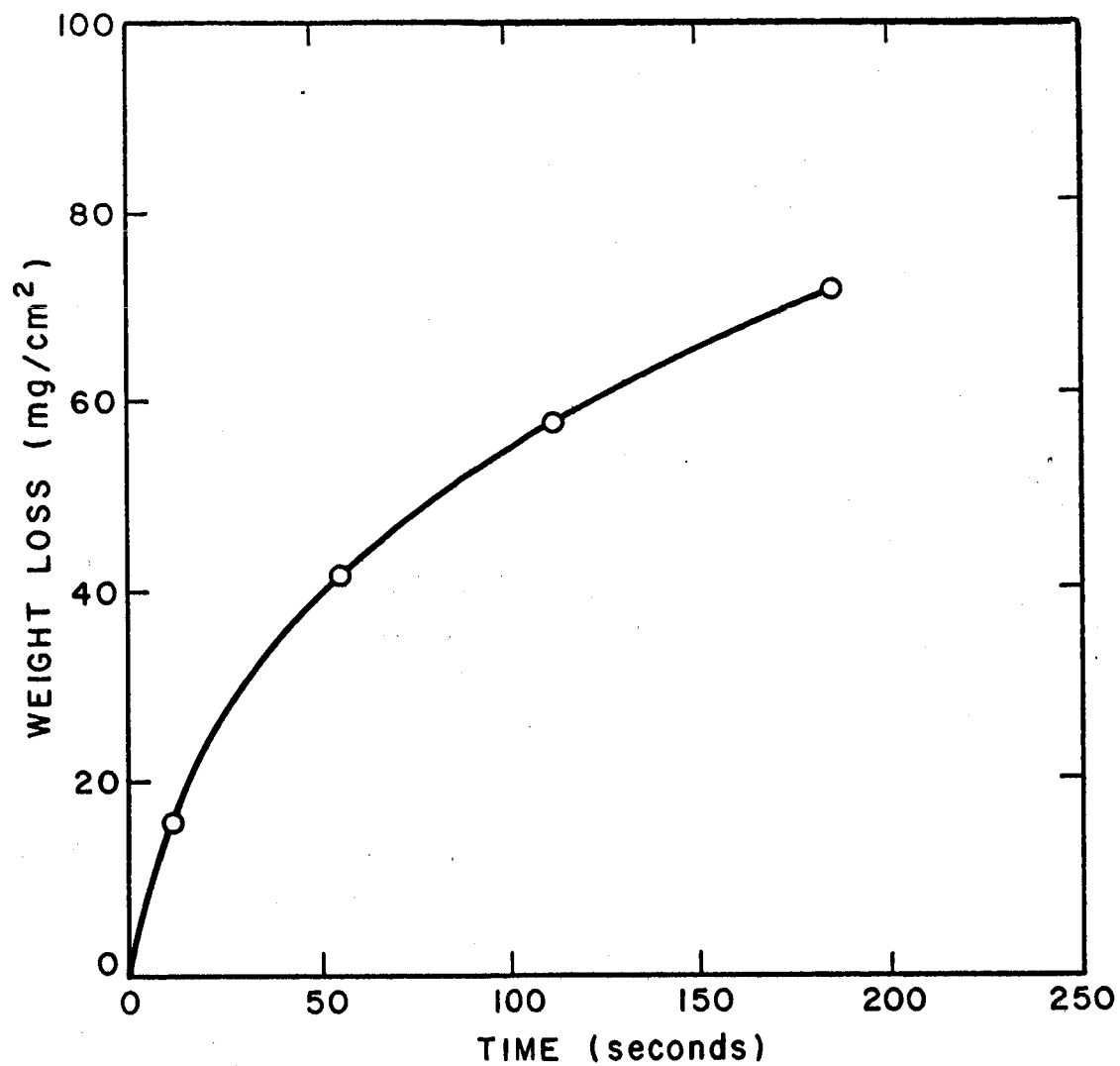
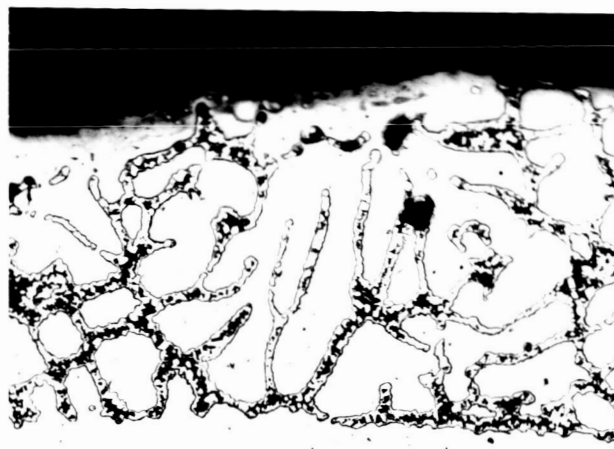


Figure 3 - Loss in weight of hafnium nitride coated tungsten heated in vacuum of 5000°F.



Neg. No. 25665

X250

Fig. 4

Structure of hafnium nitride coated
tungsten after heating in nitrogen for
5 minutes at 5000°F.

Preliminary oxidation tests were run on as-deposited HfN-coated tungsten at 2200°F. These coatings lack protective capability due to the presence of continuous cracks. During the first minute of exposure, growths of oxides form in the cracks at several locations on the coating surface. Upon continued exposure these growths become more numerous and increase in size. Only slight discoloration of the remaining nitride surface occurs. At 3600°F the oxidation products at the defect points react with the remainder of the coating to form a liquid. After several minutes at this temperature, blistering of the nitride coating occurs.

The partially dissociated structures that are produced by heating HfN-coated tungsten in nitrogen at 5000°F appear to be crack-free and more protective. A coated specimen, destabilized in nitrogen at 5000°F for 5 min, was subsequently oxidized at 4200°F. During a three-minute oxidation exposure a protective solid oxide layer formed on the nitride which cracked during cooling from the test temperature. A photograph of the cracked oxide layer appears in Figure 5.

Similar coatings, produced on Ta-10W with an intermediate tungsten layer, were oxidation tested under identical conditions and found to fail rapidly accompanied by the formation of a liquid oxidation product. Metallographic examination of the coating showed that in all cases, reaction occurred between the surface coating and the tantalum alloy due to discontinuities in the tungsten diffusion barrier. This may be seen in Figure 6.

B. Plasma-Sprayed Oxide Coatings

1. Introduction

The objective of this phase of the program has been to produce mechanically and chemically stable air-impermeable (closed pore) oxide coatings by the plasma-spray process. For this purpose, the parameters that control the properties and structure of sprayed refractory oxide and oxide-metal composite coatings have been studied. Initial work consisted of producing coatings on flat plates suitable for torch test evaluation. Ultimately, these results will be extended to produce oxide-coated refractory metal composite nozzles by spraying onto mandrels.

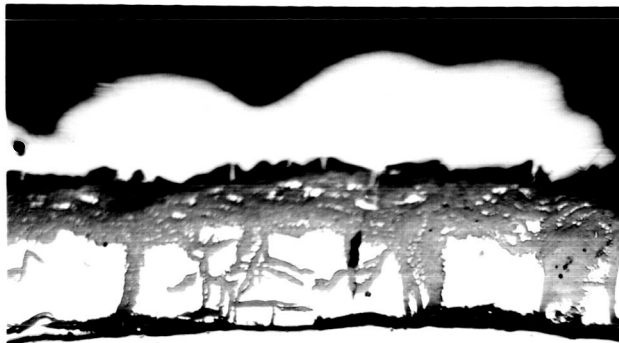


Neg. No. 24406

~ 5X

Figure 5

Hafnium nitride coated tungsten rod oxidized for 3 minutes at 4200°F after having been partially dissociated in nitrogen at 5000°F for 5 minutes.



Neg. No. 24669

X150

Figure 6

Hafnium nitride coated Ta-10W with a tungsten interaction barrier after oxidation at 4200⁰ F for 3 minutes. Reaction has occurred between the base metal and coating due to flaws in the tungsten barrier layer.

2. Background to Experimental Approach

a. Previous Plasma-Spray Coating Work

Lockheed⁽⁷⁾ has studied plasma-sprayed 10 to 30 mil coatings of ZrO_2 , HfO_2 , ThO_2 , BeO , ThB_4 , and HfB_2 on 2 x 2 x 1/8 inch plates of FS-82 alloy (Cb-33Ta-0.75 Zr), W-1ThO₂, Ta-10W, and pyrolytic graphite. The coatings were tested with a high-energy arc-plasma in a simulated air environment. The maximum average temperature in the center of the specimen was 3600°F. Reportedly, most of the coatings show first signs of failure within the first minute of exposure. Generally, the oxides failed by cracking and the borides failed through oxidation. Failure of the boride coatings was usually less catastrophic and, although liquid oxidation products were formed, there was a tendency for them to be retained on the surface of the sample.

In studying plasma-sprayed coatings for solid-propellant graphite rocket nozzles, Harvey Aluminum⁽⁸⁾ applied 3 to 5 mils of tantalum and a cover coat of about 30 mils of 50 HfO₂-50ThO₂ mixture. Indications were that the 50 HfO₂-50ThO₂ mixture would have a melting point above 5400°F, and initial tests showed the coating to have good thermal-shock resistance in contrast to the poor thermal-shock resistance of pure ThO₂.

Plasma-sprayed coatings of ZrO_2 , HfO_2 , and ThO_2 on tungsten were studied at Solar.⁽⁹⁾ A 30-mil coating of HfO₂ (stabilized with 5 weight per cent Y₂O₃) on tungsten was exposed to a plasma flame and provided oxidation protection for five minutes at 4000°F. Also, a coating of 14 mils of graded W and ThO₂ with a 20-mil cover coat of ThO₂ provided oxidation protection at 4000°F, but there was some evidence of an interfacial reaction.

From an oxidation test (30 seconds at 3000°F) of plasma-sprayed refractory carbides, General Electric Company⁽¹⁰⁾ reported that the oxide flaked off both ZrC and HfC after the first run, a 90HfC-10ZrC coating had a fairly adherent oxide, while 70ZrC-30HfC had a smooth, glassy, adherent oxide after three runs. Densities of the sprayed ZrC and HfC were 97.2 and 91.9% of theoretical, respectively. In the study of sprayed oxides, Levinstein⁽¹¹⁾ reported 95% of theoretical density for ZrO_2 and 86.8% for HfO_2 . The value for ZrO_2 seemed too high, based on photomicrographs and strength tests of the material. However, Mason⁽¹²⁾ has reported plasma-sprayed ZrO_2 coatings with densities ranging from 76.8 to 97.9% of theoretical depending upon spray conditions.

In most previous work, the poor performance of the coatings can be traced to permeability, lack of interface bond strength or chemical reactivity with the substrate. Each of these factors must be overcome to produce a successful coating.

b. Discussion of Plasma-Spray Coating Parameters

The properties of the substrate influence coating adherence, which is largely affected by mechanical interactions that occur between the substrate and coating as a result of differential heating, thermal expansion mismatch, and chemical interaction. The important physical properties of tungsten, the substrate of primary interest in this program, are presented in Table IV.

Tungsten, as a substrate presents several challenging problems to the spray coating process. It has a very high coefficient of thermal conduction, a property which Moore⁽¹³⁾ reported as a major factor in determining the length of time that spray particles are viscous enough to flow after impact. The thermal expansion of tungsten is very low, making it difficult to produce refractory oxide coatings which are in compression when coating a flat surface. Its resistance to abrasion is blamed for the indications that the normal procedure of grit blasting is not an adequate surface preparation.⁽⁹⁾

The ease with which tungsten oxides are formed indicates that the spraying process should be conducted in a vacuum or in a controlled atmosphere.

Since a coating must adhere in order to protect the substrate, much of the philosophy behind various flame and plasma spraying techniques falls into the category of coating-substrate adherence. In recent years, investigations have been conducted on a variety of coating-substrate combinations trying to isolate the effects of substrate preparation, substrate temperature during spraying, thermal expansion mismatches, and substrate-coating interactions on the bond strength. Primary bonding is considered to be mechanical^(13, 14) with reported tensile bond strengths in the range of 100 to 1000 psi.^(15, 16) However, the values for tensile bond and shear bond strengths have been increasing with continued investigation, implying that

TABLE IV
PHYSICAL PROPERTIES OF TUNGSTEN

Melting Point: 6170°F (ref. 27)

Density: 19.3 gm/cc (ref. 27)

Coefficient of Thermal Expansion (ref. 27):

<u>Temp., °F</u>	<u>in/in/°F (x 10⁻⁶)</u>
77-930	2.52
77-1830	2.65
77-2730	2.83
77-3630	3.01
77-4530	3.28

Thermal Conductivity (ref. 9,
compiled from four sources):

<u>Temp., °F</u>	<u>Thermal Conductivity, Btu/hr ft °F</u>			
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
70	75.0	96.5	95	--
1830	65.1	--	65	66
3630	--	--	60.5	--
2910	60.5	--	--	61

a chemical bonding component may be present. Wheildon et al., ⁽¹⁶⁾ and Bliton and Rechter ⁽¹⁷⁾ showed the advantage of using a metal undercoat in promoting tensile bond strength. Bliton ⁽¹⁸⁾ determined the tensile bond strength of commercially prepared zirconia coatings produced by the Rokide (rod spray), the Flame Ceramics (powder spray), and the plasma (powder spray) process, and reported strengths in the range of 1100 to 1500 psi. In evaluating coatings (thermal shock and tensile bond tests) for the X-15 rocket plane engine, the University of Dayton ⁽¹⁹⁾ determined tensile bond strengths ranging from an average of 1450 psi for one coating procedure to 3300 psi for another. The known differences in procedure were thickness of the metal subcoat, (sprayed Mo) and the thickness and effectiveness of the Nichrome-ZrO₂ dispersion in the graded coating layer.

Using coating-substrate shear bond strength as his criterion, Leeds ⁽²⁰⁾ has investigated the effect of various surface preparation and spraying techniques on the system of tungsten sprayed on mild steel. He concludes that bonding of plasma-sprayed coatings is accomplished primarily by chemical means. Bliton ⁽¹⁸⁾ reported tensile bond strengths in excess of 4100 psi with some values as high as 6000 psi for barium ferrite coatings sprayed on Inconel. The coatings were flame-sprayed while the substrate was above 1200°F. Both Leeds and Bliton have reported the ability, by one technique or another, to form adherent coatings on smooth substrates.

Except for a few isolated reports about the ability to obtain suitable bond strength by spraying on smooth surfaces, it is generally accepted that the substrate should be roughened in order to promote mechanical adherence between the coating and the substrate. In commercial practice and in many laboratories this is accomplished by a sandblasting technique usually incorporating metal chips or silicon carbide as the blasting medium. Leeds ⁽²⁰⁾ suggests that the decomposition of SiC entrapped in the substrate has an adverse effect on coating properties. Laszlo ⁽²¹⁾ developed preferential etching techniques for some metal substrates, producing a roughened surface with individual grain protrusions or peaks, but did not present bond strength data for plasma-sprayed coatings over such surfaces. The investigators at Solar ⁽⁹⁾ felt that the grit-blasting technique was not sufficient for good bonding with tungsten as the substrate. To overcome this deficiency, they

investigated electrolytic etching techniques and reported some improvement in adherence for thoria sprayed on tungsten.

Although other factors are probably involved, sprayed metal sub-coats aid in producing "keying" sites for coating attachment to the substrate and, as has been mentioned, improve adherence.

The differential thermal expansion between coatings and substrates has been an important consideration in producing adherent porcelain enamel coatings for many years. Jones and Andrews ⁽²²⁾ state that practically all satisfactory porcelain enamel or vitreous coatings are in a state of appreciable biaxial compression at room temperature. This condition is desirable to a certain degree, since such brittle materials as enamel glass are characteristically stronger in compression than in tension. From their experimental results they reported that in a commercial ground coat on 20-gage enameling iron, a compressive stress of about 35,000 psi is present in the enamel.

In the majority of coating-substrate combinations the substrate has a higher coefficient of expansion than the coating. This means that the coating will be placed in compression as the system cools. It also means that if the substrate temperature is continually increasing during the coating process, the coating already produced may form tensile cracks due to the more rapid expansion of the substrate. In some cases this can be overcome by preheating the substrate and maintaining a constant substrate temperature during spraying.

From the standpoint of trying to place the sprayed coating in compression, tungsten presents a unique problem, for while most coated substrates have a thermal expansion greater than that of the coating, tungsten has an expansion coefficient lower than the refractory oxide coatings. This lower substrate expansion tends to place the coatings in tension causing tensile cracks upon cooling. ⁽²³⁾

A number of investigators have recently attempted to overcome thermal expansion mismatch ^(19, 24, 25) by using spraying mixtures of metals and oxides and decreasing the metal-to-oxide ratio in successive coatings until the top layer is pure oxide. Kingery ⁽²⁶⁾ investigated the systems of pressed and sintered mixed powders of W and MgO and of Al and

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SiO₂. He reported that the thermal expansions are not simply averages of the end-members, but that experimental data agree quantitatively with calculations based on the assumption of residual microstresses resulting from restraint of each phase upon cooling. Table V lists the coefficient of linear expansion, extrapolated from a graph for the W-MgO bodies.

3. Selection of Coating Materials

In a recent review of the literature for coatings to protect tungsten and tantalum for re-entry applications, Solar Aircraft Co. ⁽²⁷⁾ reported the oxides, borides, carbides, and nitrides with melting points above 4500°F. After rejecting compounds which form oxides with melting points below 4000°F, the materials listed in Table VI remain. For the present program, MgO has been rejected because of its high vapor pressure at higher temperatures ⁽²⁷⁾ and its reactivity with tungsten. ⁽⁴⁾ Beryllium oxide has been rejected because of its low melting point and recently reported allotropy. Of the remaining materials, only the carbides and graphite are solid above 6000°F. However, with no reliable protective system available for tungsten above 3500°F, the oxides should not be ruled out on the basis of melting points below 6000°F. In fact, a realistic approach would be to investigate these systems first in intermediate temperature ranges.

Melting point alone cannot determine the materials selection for a coating system; coating oxidation rate, oxygen diffusion rate, and reactions with the substrate should also be considered. Oxidation rates for the carbides and nitrides are not clear from the literature but seem to warrant investigation.

The diffusion rate of oxygen through the oxides has also received little attention. However, investigations of this nature are being conducted, not for aerospace oxidation protection systems, but as oxygenion transfer membranes for solid electrolyte fuel cell applications. Kingery ⁽²⁸⁾ has measured the diffusion coefficients for oxygen through lime-stabilized zirconia and also reported that the electrical conductivity was essentially due to this diffusion. Until gas-impermeable coatings can be produced from refractory oxides, the influence of oxygen diffusion through the crystal structure cannot be satisfactorily established.

TABLE V

COEFFICIENT OF THERMAL EXPANSION
FOR TUNGSTEN-MAGNESIA COMPOSITIONS*

Composition, w/o	Coefficient of Expansion, $\times 10^{-6} / ^\circ\text{F}$
Tungsten	2.5
W-25MgO	5.0
W-50MgO	6.4
W-75MgO	6.7
MgO	7.3

* Ref. 26 data for 212° to 1830°F. Values reported here are approximate, original data in graphic form.

TABLE VI
REFRACTORY MATERIALS
AND MELTING POINTS(27)

Material	Melting Point °F
Pyrolytic graphite	6560*
HfC	7025
ZrC	6890
HfN	5990
ZrN	5390
ThO ₂	5825
MgO	5070
HfO ₂	5020
ZrO ₂	4850
BaZrO ₃	4880
SrZrO ₂	4880
BeO	4620

* Sublimes.

Although there have been recent reviews of the thermal expansion literature, (8, 9, 29, 30) there still seems to be materials for which data are not available. This is especially true of high-temperature (2500° - 4000° F) information. The data reported here have been gathered from a number of sources, and in cases where the information was compiled by a literature search, only that reference is given. Many of the values have been taken from published graphs and other data; thus the values should be taken as approximations.

The complexity and importance of the stabilization of zirconia and hafnia have caused these materials to be discussed in detail. Reported thermal expansion values for tungsten and tantalum and some refractory materials of interest as coatings are listed in Table VII.

Zirconium oxide and hafnium oxide have such similar chemical-physical properties that one in the other is difficult to detect and remove. Commercial grades of zirconia generally contain 2 to 4 per cent hafnia while commercial hafnia contains approximately the same 2-4 per cent level of zirconia. Both materials have a monoclinic crystal structure at room temperature; however, upon heating, zirconia goes through a phase change from monoclinic to tetragonal at approximately 2180° F. This is accompanied by a 3.2 per cent reduction in the length of the piece; upon cooling, a sizable length increase takes place at about 1875° F. The monoclinic-to-tetragonal inversion in hafnia occurs at about 3140° F and is accompanied by a moderate shrinkage which is believed sufficient to cause cracking during transformation. (27) For this reason, both oxides are "stabilized" in a cubic structure resulting from the solid solution with various refractory oxides; calcia (CaO) and yttria (Y_2O_3) are presently the most common stabilizers.

Since the thermal expansion characteristics of either ZrO_2 or HfO_2 are dependent upon the degree of stabilization (i.e., per cent cubic vs. per cent monoclinic), the amount of alloying oxide added affects the thermal expansion of the material. The cubic materials do not undergo any crystal inversions with temperature and have nearly linear thermal expansion curves. The coefficient of expansion is higher for the cubic structure than for the monoclinic; therefore, to impart better thermal shock properties by lowering the expansion coefficient, a compromise or partially stabilized material with

TABLE VII
REPORTED THERMAL EXPANSION DATA
FOR REFRACTORY MATERIALS

Material	Temperature Range °F	Coefficient of Expansion, $\times 10^{-6}/^{\circ}\text{F}$	Reference
Tungsten	77-3630	3.01	27
	77-4530	3.28	27
Tantalum	85-3000	3.74	9
	85-3800	4.20	9
	85-4600	5.15	9
Barium zirconate	77-1830	4.72	31
Strontium zirconate	77-1830	5.34	31
Calcium hafnate	77-1830	4.05	31
Zirconium carbide*	70-1830	4.23	29
Hafnium carbide*	70-1920	4.04	29
Thoria	212-2250	5.36	31
	80-2000	5.90	31
	77-1830	5.0	31
	77-2730	5.66	27
	77-3090	5.81	27
	70-4000	6.00	

* Plasma-sprayed coatings, values average of heating and cooling

an expansion lower than the fully cubic structure is sometimes employed. To do this, the stabilizing oxide addition is held below the level necessary for complete conversion to the cubic structure, but it is sufficient to reduce the monoclinic content to a point where the volume change during heating and cooling does not destroy the structure. Table VIII lists some expansion data for stabilized hafnia and zirconia.

Yavorsky⁽³¹⁾ reported nearly a 15 per cent reduction-- 4.95×10^{-6} in/in/ $^{\circ}$ F vs. 5.8×10^{-6} in/in/ $^{\circ}$ F--for partially stabilized (3 weight per cent) Zirconia as compared to the fully cubic (5 weight per cent CaO) material. Levinstein⁽¹⁰⁾ reported partial destabilization of lime-stabilized zirconia during the plasma-arc spray process and determined the thermal expansion of the plasma-sprayed coating to be 1.5 in/in/ $^{\circ}$ F lower than a pressed and sintered, fully cubic, piece (see Table VIII). In a literature search, Solar⁽⁹⁾ referenced two investigators' work on hafnia with and without CaO additions. The two sets of data varied by 30 to 100 per cent, with one set of values being very close to the coefficient of expansion of tungsten. Solar⁽²⁷⁾ then conducted thermal expansion measurements to clarify the discrepancy. Data for hafnia with 0, 5, 10 and 15 weight per cent additions are listed in Table VIII along with values obtained for yttria-stabilized zirconia and thoria. The coefficients listed in Table VIII do not tell the whole story because the unstabilized and partially stabilized (0 and 5 weight per cent additions of Y_2O_3) hafnia did not have smooth expansion curves. The discontinuities did not seem to be enough to seriously damage the test pieces. The main importance of this work was the fact that the unstabilized and partially stabilized materials had coefficients of expansion approximately 50 per cent lower than the fully stabilized (10 and 15 weight per cent yttria) hafnia. The expansion of cubic hafnia was similar to that of cubic zirconia and thoria.

4. Equipment and Procedures

a. Spray Equipment

The plasma spray unit used throughout this program was a Plasma-dyne SG-3 model rated at 25 kw. Figure 7 shows the torch mounted in the controlled atmosphere spray chamber. The mechanism for adjusting the torch-to-substrate distance can also be seen in Figure 7. The apparatus, which moves the specimen across the spray path of the stationary torch,

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TABLE VIII
REPORTED THERMAL EXPANSION DATA
FOR ZIRCONIA AND HAFNIA

Material, w/o	Crystal Structure ⁺	Temperature Range, °F	Coefficient of Expansion, $\times 10^{-6}/^{\circ}\text{F}$	Reference
ZrO ₂ + 3CaO	C + M	68-2190	4.95	29
ZrO ₂ + 5CaO	C	68-2190	5.8	29
ZrO ₂ + 5CaO	C	RT-2000	5.01	11
ZrO ₂ + CaO*	C + M	RT-2000	3.49	11
ZrO ₂ + CaO*	C	70-1800	5.2	32
ZrO ₂ + 12Y ₂ O ₃	C	RT-4000	5.05	32
ZrO ₂ + 10Y ₂ O ₃	C	RT-4000	6.35	27
HfO ₂	M	RT-4000	4.0	27
HfO ₂ + 5Y ₂ O ₃	C + M	RT-4000	3.25	27
HfO ₂ + 10Y ₂ O ₃	C	RT-4000	6.5	27
HfO ₂ + 15Y ₂ O ₃	C	RT-4000	6.30	27

⁺ C = cubic, M = monoclinic

* These samples were plasma-sprayed.

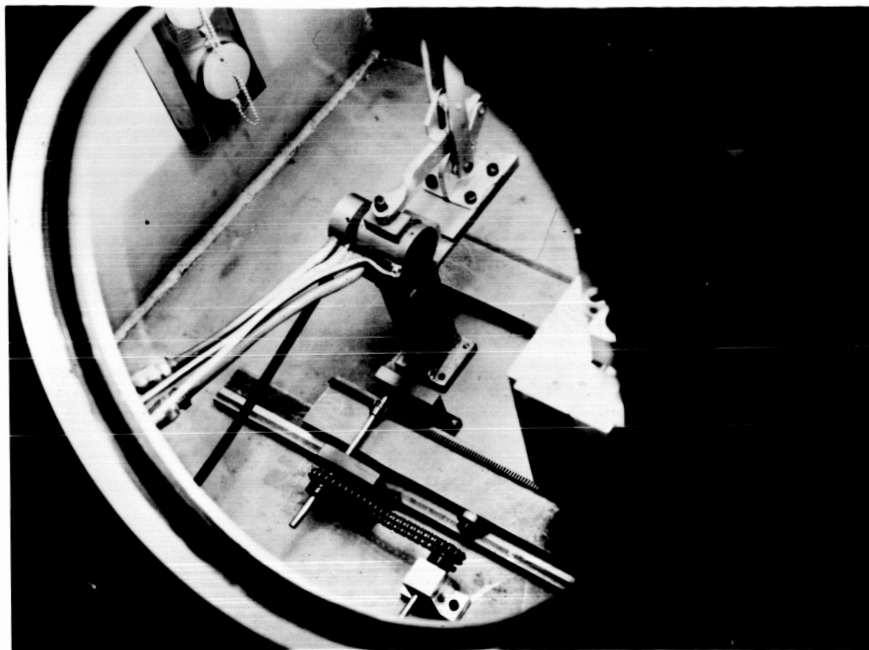


Figure 7

View downward through front observation port of dry box showing torch, in center, and torch-to-specimen distance-adjusting device.



Figure 8

Sample-moving device mounted in the controlled-atmosphere chamber.

incorporates independent and variable-speed horizontal, vertical, and rotational movements, and is shown in Figure 8. In this figure, the spray torch is mounted behind the reflector plate (left-center). The chuck shown on the specimen mover is for a single 3/4-inch diameter sample. Other chuck designs which were used allowed coating of six 3/4-inch diameter cylinders at one time or coating of plates up to 3 x 3 inches. Figure 9 depicts the spray complex, with the torch control console on the left, two feed hoppers in the center, and the controlled-atmosphere spray chamber on the right. Specimen temperatures were determined with a Thermodot radiation pyrometer sighted through a quartz window.

The powder feed unit used was a Continental Coatings Corporation feed hopper which consisted of a pressurized powder reservoir with a variable-speed screw exit parallel to and near the bottom. When the powder has been carried clear of the reservoir, a vertical stream of gas cleans the screw and the particles become airborne. The gas bearing the powder passes through a mixing chamber and enters the feed hose connected to the torch.

For this program, two units were modified so that the vertical gas take-off carried the powder down instead of up and the hoppers were attached to a common gas-powder mixing chamber. The standard No. 6 pitch feed screws were replaced with No. 8 pitch screws which carried less powder per trough but deposited powder in the gas stream more frequently, thus eliminating a powder spurting effect.

The feed system was such that one hopper operated at a time, but the change from one to the other took 15 to 20 seconds and could be accomplished while the torch was operating.

b. Powder Selection and Spray Parameters

The deposition of a sprayed coating with a noncontinuous pore structure demands precise control over a number of variables, most of which are dependent upon the physical characteristics of the powder to be sprayed. To arrive at the right powder and accompanying processing methods, it is necessary to examine the coating formation process.

The voids present in most coatings are the product of poor particle packing and lack of particle deformation. The amount of particle deformation

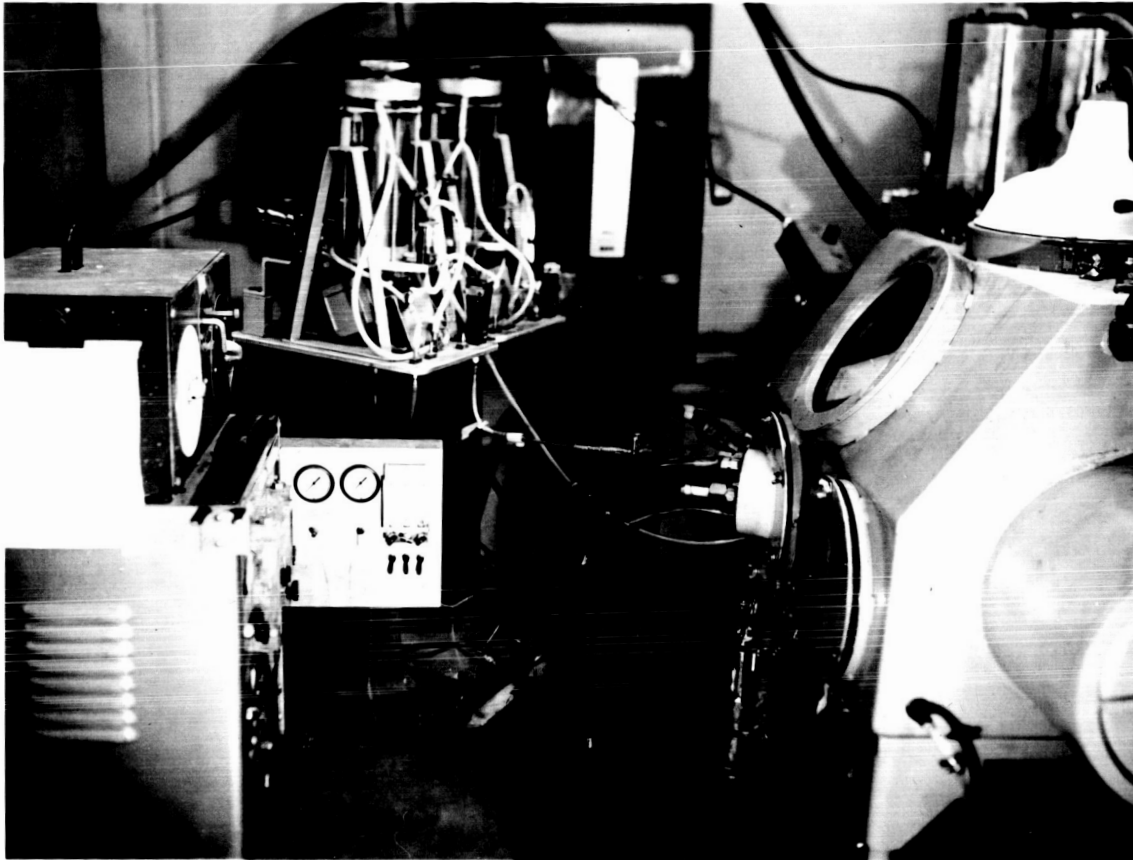


Figure 9

Plasma spray unit, showing the controlled atmosphere spray chamber, two feed hoppers, and the plasma jet control console.

that occurs during spraying is influenced by the particle mass, velocity, temperature at the time of impact, and the quenching propensity of the substrate. For any specific material the particle size determines its heating and cooling rate. Size also influences the velocity⁽³²⁾ and the impact force. For uniform deformation, then, the particle size should be as uniform as possible. The selection of the actual particle size is based on a compromise of the ability of the particles to project in a straight line, to be uniformly heated, and to deform properly upon impact. For this program a fine particle size, 10 to 25 microns, was selected.

Another point to consider is that of controlled deformation. Moore⁽¹²⁾ has shown that molten particles hitting a smooth surface at too high an impact force splatter and atomize, causing the expulsion of very fine droplets that chill rapidly. Previous studies at IITRI show that such conditions can cause void formation, and that the chilled droplets intersect the path of the oncoming particles. Also, as in conventional ceramic forming techniques (hot pressing or forming and sintering), the void structure and particle-to-particle bonding is influenced by the particle time-at-temperature after impact. Moore⁽¹²⁾ suggested that quench rate of a molten alumina particle striking a stainless steel plate would be of the order of 8×10^5 °C/sec which indicates a time for flow of approximately 0.001 seconds. He also indicated that this quench rate was dependent upon the thermal conductivity and the temperature of the substrate. Bliton⁽¹⁸⁾ showed that preheated substrates (1200°-1900°F) did not cause deformation of poorly heated spray particles; however, the use of hot substrates with properly conditioned particles caused void reduction and high-strength particle-to-particle bonding.

The spray work on this project was conducted in accordance with these established ground rules.

c. Spray Powders

Upon heating, ZrO_2 goes through a crystal phase change from monoclinic to tetragonal at approximately 2180°F. This is accompanied by a 3.2 per cent linear shrinkage. Upon cooling, a large expansion occurs at about 1875°F as the material reverts back to the monoclinic form. These inversions are sufficient to shatter bodies formed of monoclinic zirconia.⁽³¹⁾

For this reason, zirconia is alloyed with a "stabilizing agent" to form a cubic structure which does not transform allotropically during heating and cooling. Calcia (CaO) and yttria (Y_2O_3) are presently the most common stabilizing agents.

Previous work on dense sprayed coatings has shown a commercially available lime-stabilized zirconia powder to be an acceptable spray powder. This material, Zircoa* (-20,+5 micron GGB zirconia powder), had a reported particle size range of 80 per cent in the 20 to 5 micron range. A typical analysis of the powder is presented in Table IX. To insure uniformity of the material, the as-received powder was calcined at 1200°F for 4 hours to remove any carbonaceous material introduced during manufacturing, wet-screened -400 mesh (30 microns) to remove possible agglomerates, and water-elutriated to remove any particles smaller than 5 microns. The processed powder had a particle density of 5.23 g/cc, as determined by an alcohol pycnometer, and a mean particle size diameter of 14 microns with a standard deviation of 1.75 microns, as determined by the Andreason pipette technique. X-ray analysis showed the crystal structure to be fully cubic.

Unless otherwise stated, this material is the zirconia referred to in this report.

The second zirconia powder which was investigated was yttria-stabilized zirconia, of fine particle size, designated as R75236D by the manufacturer.** The particles were relatively spherical and approximately 10 microns in diameter. X-ray analysis showed a single-phase cubic structure, and the material was reportedly of much higher purity than most commercial stabilized zirconia powders. Although relatively little work was done with this powder, its spray-ability was well demonstrated, as will be seen in Section 4-d.

Hafnium dioxide is very similar to zirconia in its chemical-physical properties and similarly undergoes a monoclinic to tetragonal crystal inversion which occurs at about 3140°F . This inversion is accompanied by a moderate shrinkage which is, however, still sufficient to weaken the structure of dense bodies going through the transformation.⁽³¹⁾

* From Zirconium Corporation of America, Solon, Ohio

** Titanium Alloy Manufacturing Division of National Lead Company, Niagara Falls, New York

TABLE IX
TYPICAL CHEMICAL ANALYSIS
OF ZIRCONIA FLAME-SPRAY POWDER*

Constituent	Weight Per Cent
ZrO ₂ (normal HfO ₂ Type)	92.50
CaO	5.33
MgO	0.63
SiO ₂	0.37
Al ₂ O ₃	0.50
TiO ₂	0.30
Fe ₂ O ₂	0.20

* Zircoa (-20, +5 micron GGB zirconia powder)
supplied by Zirconia Corporation of America,
Solon, Ohio

Hafnia can be stabilized to a cubic form by alloying with Y_2O_3 . The coefficient of expansion of the cubic material is nearly linear and is higher than that of the monoclinic. Therefore, to improve thermal shock resistance by lowering the expansion coefficient, partially stabilized material with an expansion lower than fully cubic is sometimes employed. This is accomplished by maintaining the composition of Y_2O_3 at a level below that necessary for complete conversion to the cubic structure, but sufficient to reduce the monoclinic content to a point where the volume change during heating and cooling does not destroy the structure.

Solar Aircraft ⁽¹⁶⁾ reported the linear thermal expansion of 5 w/o yttria-hafnia to be approximately 50 per cent lower than that of fully cubic 10 w/o yttria-hafnia and therefore much closer to the expansion of tungsten. Thus, the powder investigated on this program was a 5 w/o yttria-hafnia material.

The powder investigated was received from Zircoa and was approximately 80 per cent in the +10, -25 micron range, as determined by the Coulter Counter technique. X-ray analysis showed the material to be primarily cubic but with the definite presence of the monoclinic phase. The density of the powder, as determined by an alcohol pycnometer, was 8.43 g/cc.

Typical analysis supplied by Zircoa showed the yttria addition to be 99.99% Y_2O_3 and the hafnia (containing approximately 2% zirconia) to be 99.2 to 99.5% pure. This is the material referred to as hafnia in the remainder of the report.

There are even fewer data available for strontium zirconate than for hafnia. However, its reported melting point of 5000°F and the information that it was readily sinterable to form a dense body ⁽³²⁾ indicated it was worthy of investigation. Thermal expansion data showed an expansion near that of cubic zirconia and no inversion nonlinearities. ^(32, 12)

The powder used for this investigation was supplied by Zircoa and had a particle size range with 90 per cent between 10 and 25 microns (determined by a Coulter Counter). X-ray analysis showed the material to be single phase.

Two particle sizes of tungsten powder were required for the project: a fine powder to be compatible with the spray conditions established for the 10 to 25 micron oxides, and a larger grit material for use as an adherence-promoting undercoat.

The powder selected to be sprayed with the oxides was grade M 55 from Sylvania Electrical Products, Inc., * with a reported average diameter of 5.5 microns (Fisher No.). A microscopic examination showed most of the material to be in the 3 to 8 micron range, with some large agglomerates present. The powder was dry-screened (-325 mesh) to break up or remove the large agglomerates.

The powder used for producing the adherence-promoting rough textured undercoat was -74,+44 micron (-200 mesh,+325 mesh) and was obtained from two sources, Plasmadyne** and Shieldalloy.*** The Plasmadyne material as well within the particle size range, while the Shieldalloy powder had to be screened to remove nearly 50 per cent of the material which was -325 mesh.

d. Determination of Spray Parameters

The spray parameters for the powders described were determined by first choosing the balance between the 3 v/o hydrogen-argon feed gas and ordinary argon as stabilizing gas which produced a powder feed pattern in the center of the flame, and then determining the power setting that would produce the proper particle deformation at a spray distance between one and two inches.

The amount of particle deformation upon impact was determined by the slide-distance test developed by Moore,⁽¹³⁾ which consists of placing microscope slides on end and side by side with each slide at an increasing distance from the spray torch. After one quick pass of the spray torch, the slides are examined microscopically. A typical slide which shows particle deformation is shown in Figure 10. This slide is of GGB zirconia sprayed with the parameters established for the remainder of the program; see Table X. An exception to this table was the spraying of the tensile bond specimens to be discussed later.

* Towanda, Pennsylvania

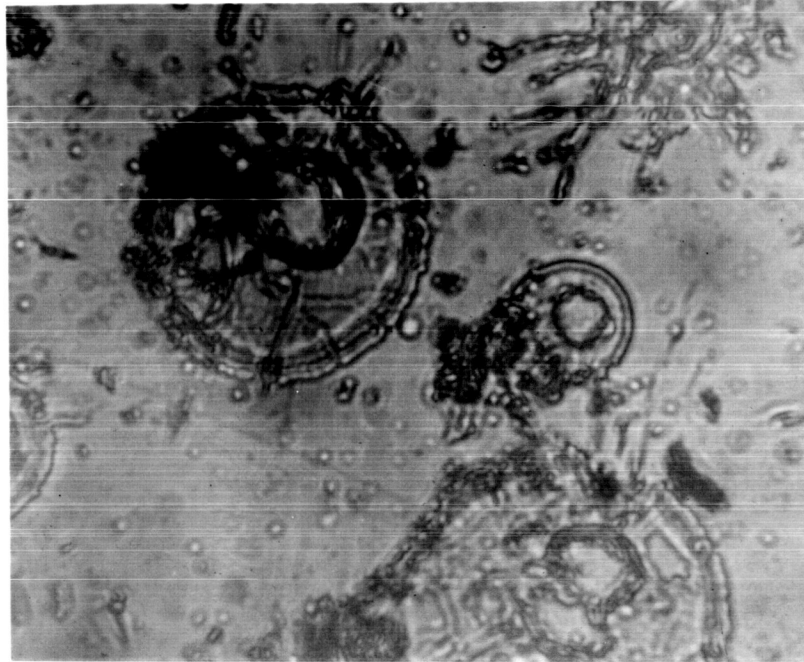
** Santa Ana, California

*** Newfield, New Jersey

TABLE X
PARAMETERS FOR PLASMA SPRAYING
IN A HYDROGEN-ARGON ATMOSPHERE

Parameter	Oxides and 5.5 μ Tungsten	-74, +44 μ Tungsten (Undercoating)
Arc-stabilizing gas	Ar	Ar
Arc gas flow (cfh)	60	60
Arc gas pressure (psi)	23	23
Feed gas *	3 v/o H ₂ +Ar	3 v/o H ₂ +Ar
Feed gas flow (cfh)	18-20	18-20
Feed gas pressure (psi)	2.4-2.7	2.4-2.7
Torch power requirements		
amps	200	350
volts	30	36
Spray distance (in.)	1.5	2.25

* At substrate temperatures above 1200°F, straight argon as the feed gas allowed discoloration of the tungsten. The 3 v/o hydrogen (pre-mixed tank gas) did not.



X1200

Figure 10

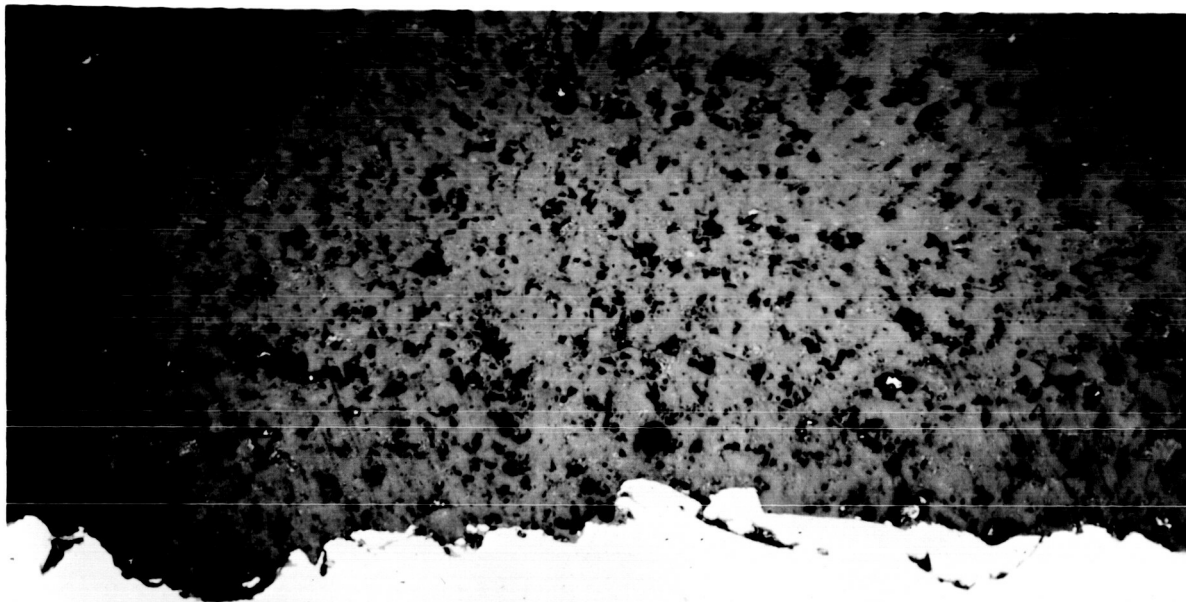
Sprayed zirconia particles in the slide-distance test.
Conditions as shown in Table X.

Photomicrographs of several coatings that were produced while determining spray parameters appear in Figures 11 through 14. Figure 11 is a lime-stabilized zirconia coating formed on a grit-blasted nickel substrate at a 1400°F substrate temperature. The specular particles seen are small pieces of tungsten that were either left in the feed system from previous tungsten runs or small pieces emitted from the rear electrode. The dark areas are voids, some of which may have been caused by tearing out of particles during polishing. The conformity to the substrate and the particle-to-particle packing were both acceptable at this stage of the investigation. Figure 12 shows an yttria-stabilized zirconia coating sprayed on an Inconel substrate at 1100°F. The void structure seems to be somewhat smaller than for the GGB spray powder. Figure 13 is a composite layer produced by spraying a mixed powder of 43 w/o tungsten-57 w/o zirconia. This shows good dispersion of the tungsten in the zirconia and very good particle deformation. Figure 14 shows a coating produced with a 20 w/o tungsten-zirconia powder; again good particle dispersion and interparticle packing is noted.

The coatings described above were all produced early in the project and were on oxidation-resistant substrates. The coatings on tungsten were produced in the controlled-atmosphere chamber in an atmosphere of 3 v/o hydrogen-argon. A check valve on the chamber maintained a positive pressure of approximately 0.5 psig. Substrate temperatures during spraying ranged from 1100° to 1800°F.

e. Coating-Substrate Adhesion Studies

The performance of a directly cemented oxide coating on a metal, of the type produced by plasma spraying, is strongly influenced by the strength of the bond formed between coating and substrate. The extent to which such bonding is chemical or mechanical in nature is a subject for much conjecture. Although various investigators have demonstrated that significant chemical bonding does occur during spray coating, it is reasonable to assume that mechanical keying accounts for a large portion of the bond strength that is observed between coating and substrate in most systems. Whether or not this is valid, it is reasonable to assume that any strength contribution due to mechanical keying should be additive to strength derived from chemical bonding. Accordingly, methods of substrate surface preparation, designed

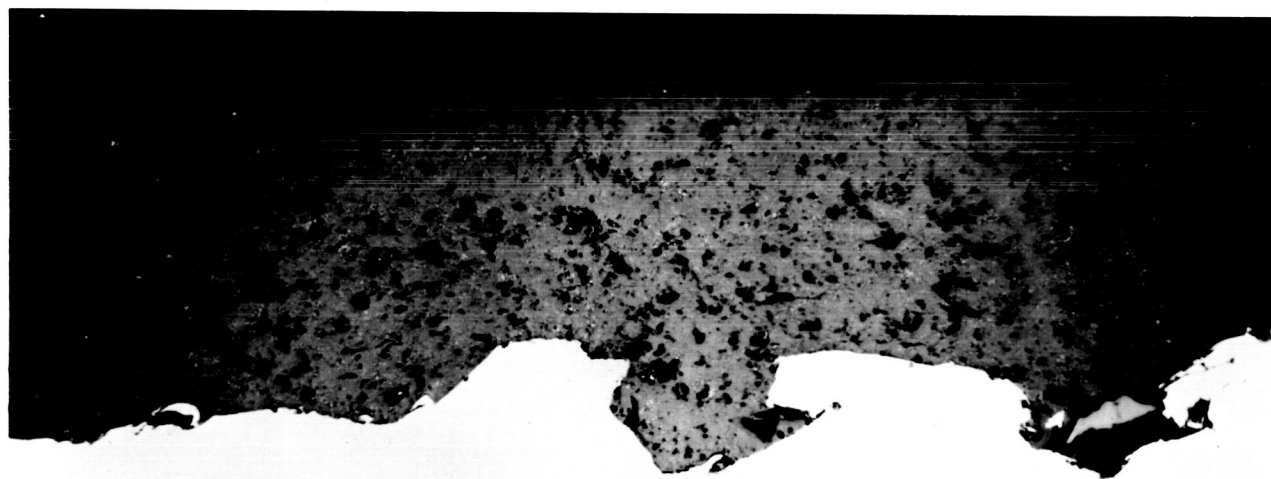


Neg. No. 23606

X500

Figure 11

Lime-stabilized zirconia on a nickel substrate.

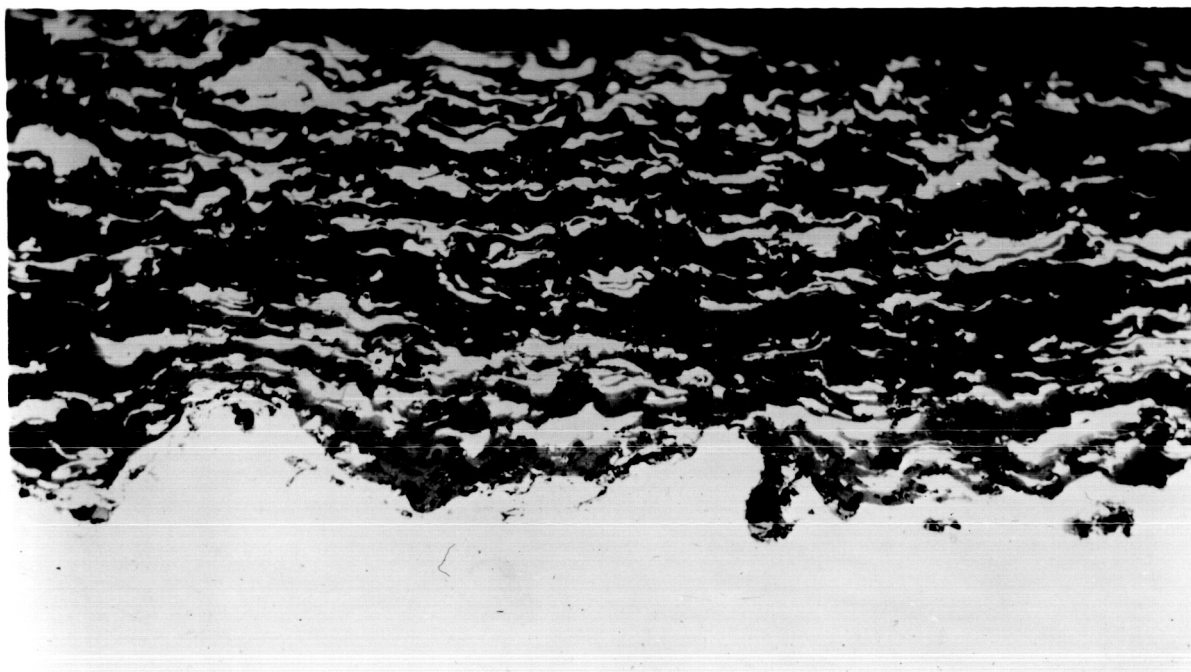


Neg. No. 23605

X500

Figure 12

Yttria-stabilized zirconia on an Inconel substrate.

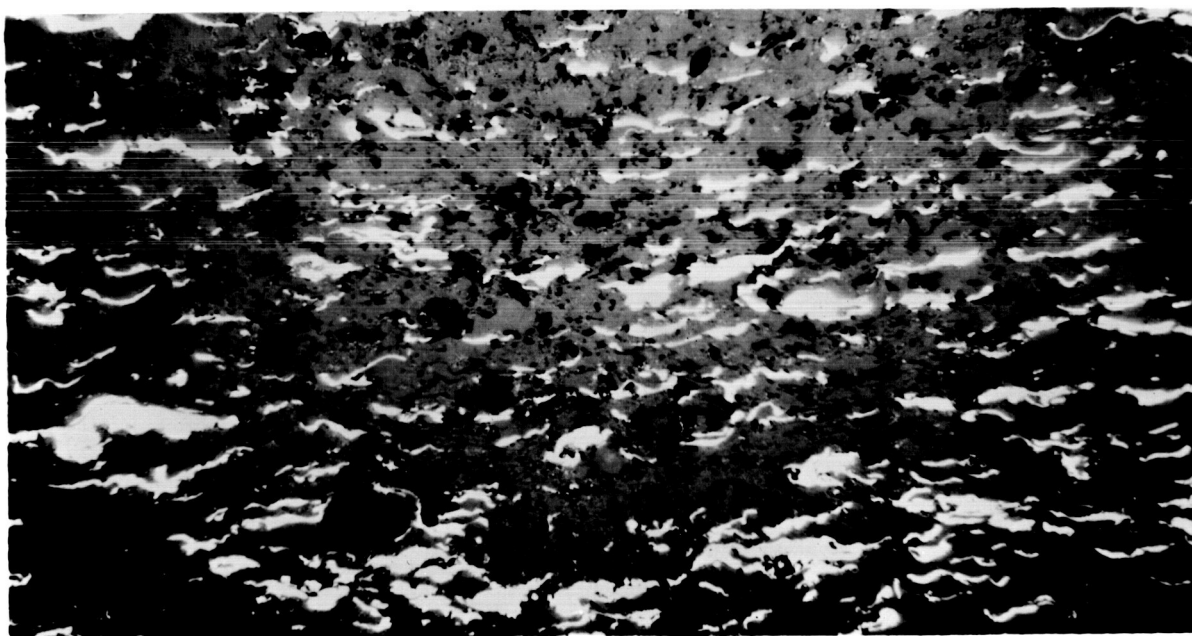


Neg. No. 23604

X500

Figure 13

Sprayed 43% tungsten-57% zirconia (by weight) composite on a nickel substrate.



Neg. No. 23603

X500

Figure 14

Sprayed 20% tungsten-80% zirconia (by weight) composite.

to promote coating bond strength through mechanical keying, were studied. These included normal grit blasting, a sprayed metal undercoat, and four electrolytically produced etch patterns (two regular patterns of peaks and two regular patterns of holes).

Two test procedures were used to measure the effectiveness of surface preparations. These consisted of a tensile bond strength measurement at room temperature and a thermal shock test: rapid heating of coated plates with an oxygen-hydrogen torch during full scale oxidation tests.

The bond strength was determined by coating one end of a 3/4-inch diameter, 3/4-inch high tungsten cylinder and then cementing* the coating surface to an uncoated 3/4-inch diameter steel cylinder which had a threaded hole in the opposite end. The tungsten cylinder was then cemented in a countersunk one-inch diameter steel cylinder drilled and threaded for attachment to the testing machine (see Figure 15). The epoxy-coated joint was filed or sanded down to insure no epoxy overlap, then the joined cylinders were stressed in tension.

The samples with only grit-blasted surfaces and those with grit-blasted and undercoated surfaces were sprayed one at a time, while the electrolytically etched samples were sprayed six in one operation through the use of a rotating wheel specimen holder developed later in the program. The spraying of the tensile bond specimens was conducted at approximately 5 kw, (1 kw lower than that used for the larger plates used for oxidation studies) in a 3 v/o hydrogen-argon atmosphere with the substrate temperature controlled as nearly as possible between 1100° and 1300°F.

Preliminary work showed that with grit-blasted tungsten and a straight oxide coating the interfacial stresses during cooling from the coating temperature were high enough to cause continual spalling of the zirconia coatings and periodic spalling of hafnia coatings. Thus in the bond strength studies, a 40% W-60% HfO₂ layer was applied prior to coating with hafnia.

All specimens tested, including those with etched surfaces, were grit-blasted prior to coating. The process consisted of blasting the samples with No. 20 grit SiC with an air line pressure of 80 psi and a blast distance of 2 inches using a bench type unit. The surfaces were then cleaned with a

* Armstrong A-12 two-joint epoxy was used, Armstrong Products Company, Warsaw, Indiana.

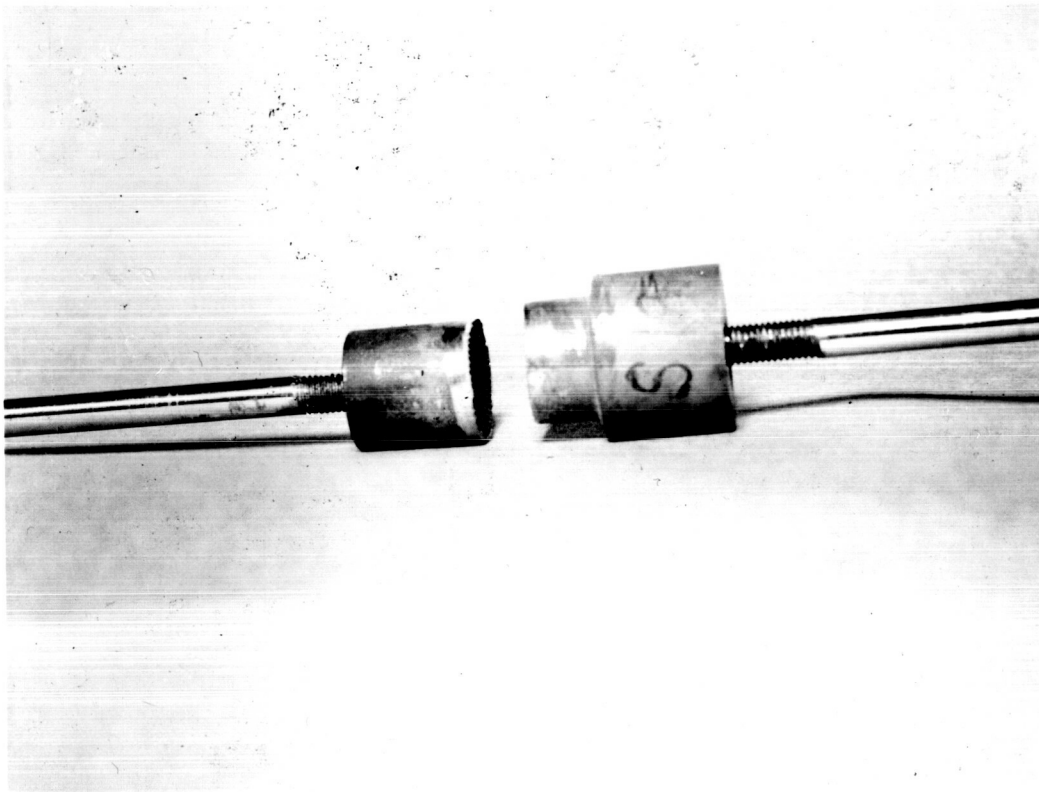


Figure 15
3/4 inch diameter tensile test specimens after testing.

stiff-bristled brush to remove lodged grit. The grit was completely changed after blasting six specimens.

A typical surface of an unetched grit-blasted surface is shown in Figure 16. Such a surface contains a large number of smooth-sided, V-shaped depressions which do not promote mechanical keying.

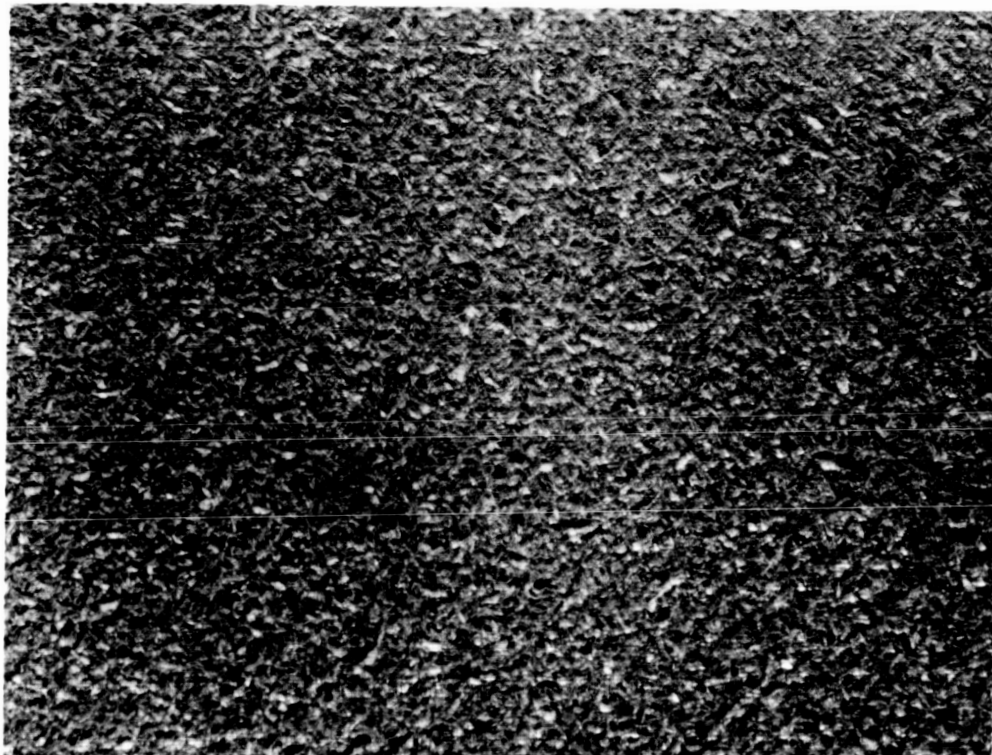
The sprayed metal undercoat is a well recognized method of increasing the width of the interfacial zone and promoting mechanical attachment of the coating. In this program, the undercoating was large grit (200 x 325 mesh) tungsten sprayed under the conditions shown in Table X to produce a rough textured surface. A typical undercoated surface is shown in Figure 17.

The photoengraving-etching process consisted of painting the tungsten with a light-sensitive organic liquid, and light-exposing the surface through a photographic negative of a dot pattern. The unexposed areas remained water soluble and were washed away, whereas the exposed areas remained in place, protecting the tungsten during the subsequent 5% NaOH-anodic etching process.

Four photographic negatives were employed, two with 25 lines/inch and two with 65 lines/inch. For a given line/inch pattern, one negative exposed the dot area, allowing etching around the spot and resulting in a truncated cone, while the other exposed the area around the dot, allowing a hole to be etched.

The etching process, as conducted, did not produce undercutting and the tungsten surface was very smooth, as can be seen in Figure 18. Thus, the etched surfaces were grit-blasted prior to being plasma-spray coated. Figure 19 shows the surface of the large truncated cones after grit blasting just prior to being coated.

Five samples were tested for each surface preparation with the exception of the fine peaks and fine holes. All failures occurred at the (40 w/o tungsten-60 w/o hafnia) tungsten interface, and the data obtained are shown in Table XI. The range of bond strength values has been reported to give an indication of data spread and the overlap of values. Past experience with this test procedure has shown that such spreads are not indicative of the test procedures itself; in fact, coefficients of variance of 2 to 8 per cent have not been

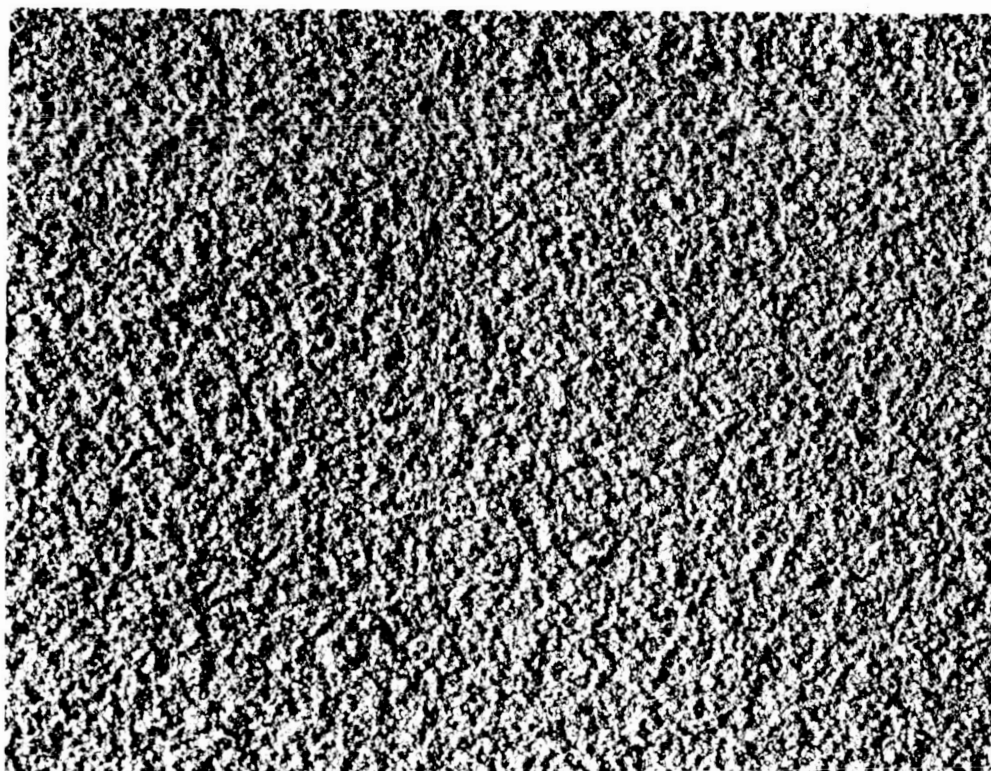


Neg. No. 23621

20X

Figure 16

SiC grit-blasted tungsten surface.

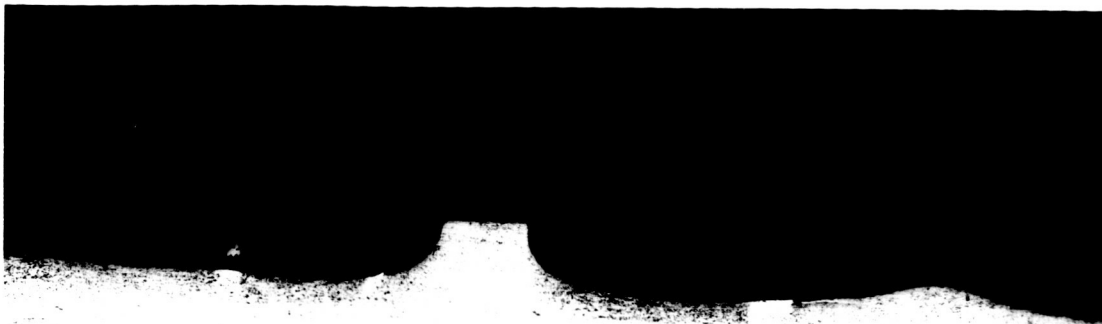


Neg. No. 24627

10X

Figure 17

-74, +44 micron tungsten sprayed on tungsten

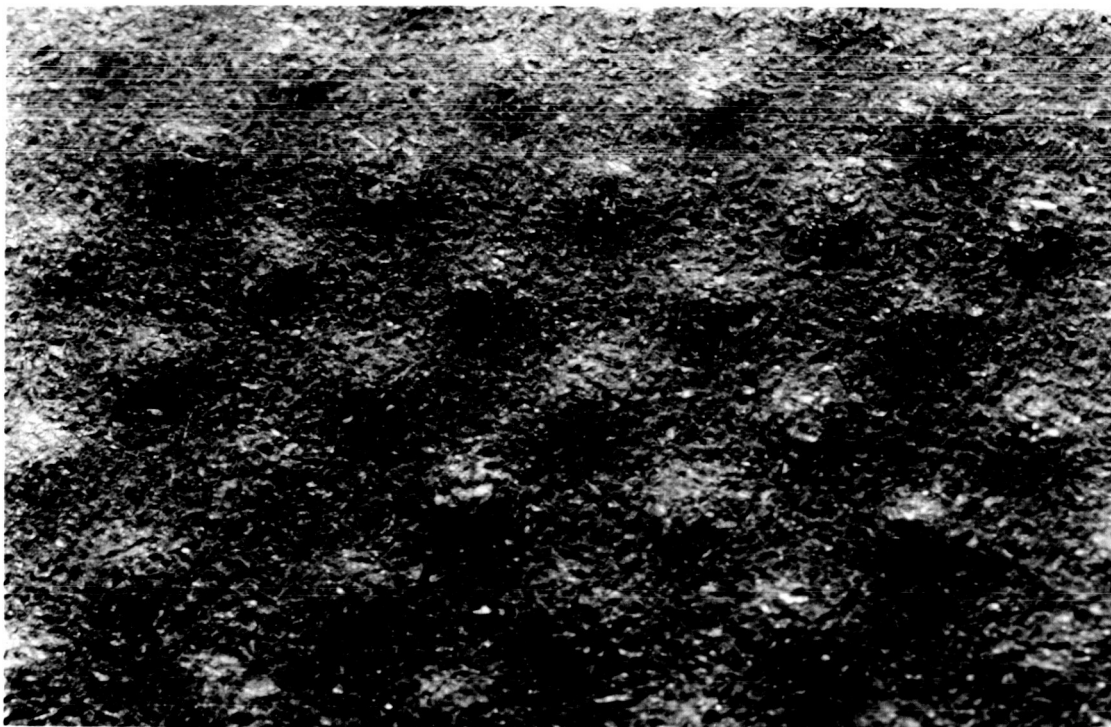


Neg. No. 24659

X100

Figure 18

Cross-section of an etched peak (65 lines/inch).
Note: No undercutting



Neg. No. 23719

20X

Figure 19

Grit-blasted larger peaks (25 lines/inch).

TABLE XI

TENSILE BOND STRENGTH DATA

FOR TUNSTEN-HAFNIA COATINGS*

ON TUNGSTEN

Surface Preparation	Tensile Bond Strength, psi	
	Range	Average
Grit-blasted	1080-2330	1770 (5 tests)
Grit-blasted sprayed tungsten subcoat	2270-2670	2420 (5 tests)
Etched, grit-blasted:		
Coarse peaks	1020-2160	1680 (5 tests)
Fine peaks	965-1250	1108 (4 tests)
Coarse holes	1700-2280	1828 (5 tests)
Fine holes	1820-2840	2330 (3 tests)

* First layer approximately 5 mils of 40 w/o W-60 w/o HfO_2 , second layer approximately 5 mils of HfO_2 .

uncommon. These data, however, indicate a lack of uniformity in surface preparation or in spray parameters such as surface oxidation, substrate temperatures prior to spraying, or random tungsten-hafnia segregation, causing more tungsten-to-tungsten contact in some samples.

The type of failure also indicates that a tensile measurement does not take advantage of the etched surface the way a shear measurement would. Figure 20 shows a "large" (25 lines/inch) etched hole substrate from which the coating seen in Figure 21 has been pulled free. Figure 21 shows bumps and is the matching surface of Figure 20. The back of the coating reproduced the surface of the holes right down to the contour of the grit-blasting marks in the hole, denoting parting at the substrate-composite interface.

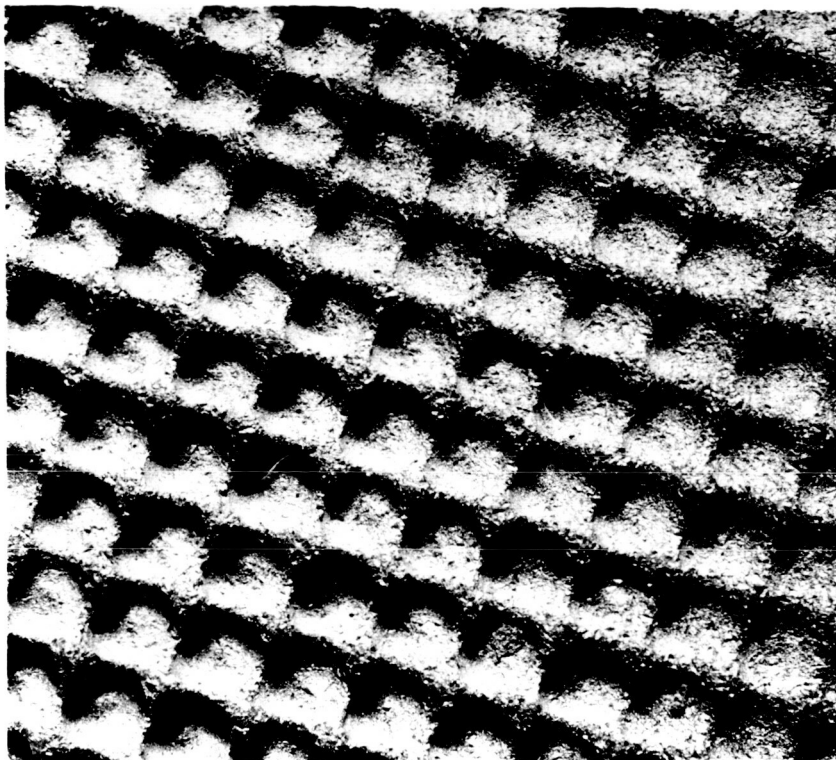
Of all the etched surfaces, only the fine 65 line/inch holes showed any appreciable gripping of the coating. Figure 22 shows the back of a coating pulled free of such a surface. As can be seen, only a few holes released the coating as the larger holes did; in most cases, the coating failed leaving the bottom of the hole filed.

The sample shown in Figure 22, which had a sprayed tungsten undercoat, failed at 2840 psi, the highest value obtained in the whole test series. This surface treatment, which was easy to prepare, had a small data spread and caused a marked increase in strength over the ordinary grit-blasted surface. The type of failure was indicative of sprayed metal undercoating with small pieces of coating remaining in the undercoat and some undercoat particles in the coating.

As has been mentioned, the sprayed undercoat was selected for the surface preparation of the 3 x 3 x 0.1 inch plates coated for oxidation testing. In these tests, sample surface temperatures were raised from room temperature to over 4000°F in approximately 15 seconds. Whereas coatings over straight grit-blasted surfaces (in early tests) were subject to interfacial failure during heating, none of the tungsten undercoated plates failed in this manner.

f. Oxidation Testing of Coated Plates

The high-temperature oxidation tests that were developed were not to simulate rocket nozzle firing conditions but to allow a quick and easy



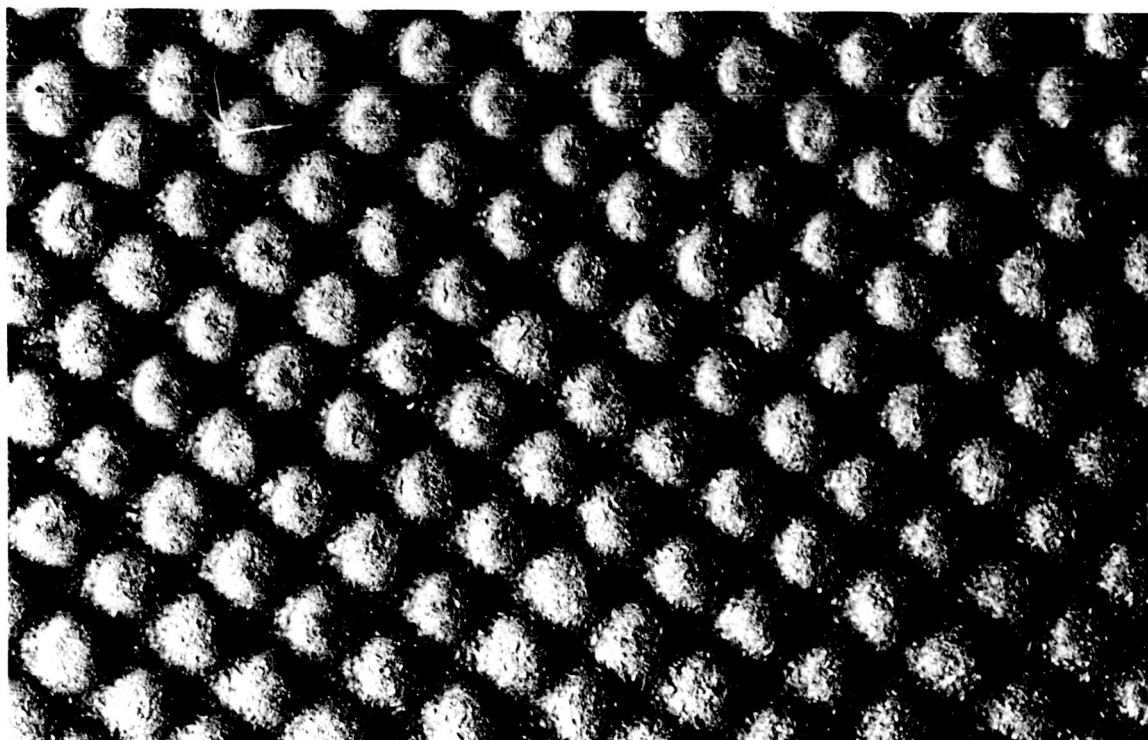
Neg. No. 2462

Figure 20

10X

Etched holes (25 lines/inch) after tensile test.

Note: The figure may appear as an optical illusion;
careful study will show a hole pattern.



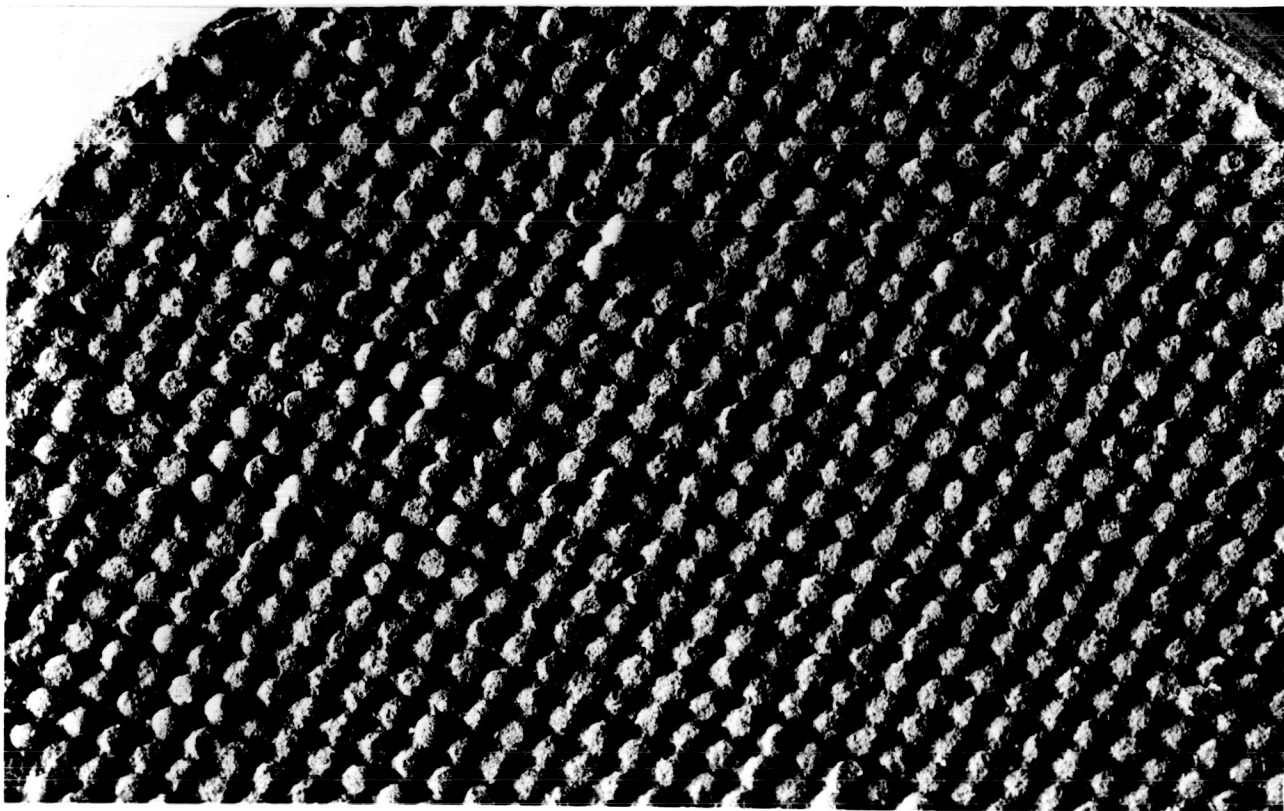
Neg. No. 24630

Figure 21

10X

Back of coating freed from surface seen in Figure 20.

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Neg. No. 24629

Figure 22

10X

Back of coating freed from "fine" (65 lines/inch) holes. Note: Most of coating nodes protruding into the substrate left the top of the node in the substrate. A few nodes pulled free, intact.

evaluation of the coating systems under study. After working with an oxygen-acetylene torch, the small SG-3 plasma torch, and an oxygen-hydrogen torch, the following torch test criteria were established:

1. The test conditions should not melt the oxide coating;
2. The test must heat a 3 x 3 x 1.0 inch bare tungsten plate above 3500°F and cause an oxidation rate in excess of 25 mils /minute;
3. The test must be capable of destroying a tungsten silicide coating in a relatively short period of time;
4. The test must produce a surface temperature in excess of 3600°F on oxide-coated tungsten plates.

A single oxygen-hydrogen torch did not meet all these requirements and a silicide coating provided protection for tungsten for at least 5 minutes under these conditions. However, this single torch test was used to evaluate preliminary coatings and provided useful information regarding thermal shock and coating design.

The final screening test developed consisted of two oxygen-hydrogen flame spray torches with barrels having 0.130 inch ID. The torches were mounted with one on top of the other, as seen in Figure 23, with flames converging at two inches, which was the test distance. Each torch was operated with 60 cfh oxygen and 120 cfh hydrogen at 25 psi gage pressure. The torches were mounted on a sliding rack so they could be ignited and gas flows corrected before striking the substrate. The samples being tested were set at an angle 40° from vertical and backed by a refractory insulating brick.

The dual torch system met all the specified test conditions including heating a bare tungsten plate to 3700°F (uncorrected optical pyrometer) and causing an oxidation rate of 48 mils/minute. Silicide-coated tungsten showed coating degradation after 20 to 30 seconds of exposure, and marked loss of the substrate occurred in less than two minutes. Surface temperatures of at least 4000°F were obtained for the oxide coatings with the time required to reach temperature being less than 20 seconds (usually close to 10 seconds).

Surface temperatures were determined with a Thermodot radiation pyrometer and an optical pyrometer. Since reliable emittance data were not available for the oxides in air at 4000°F, the uncorrected optical pyrometer

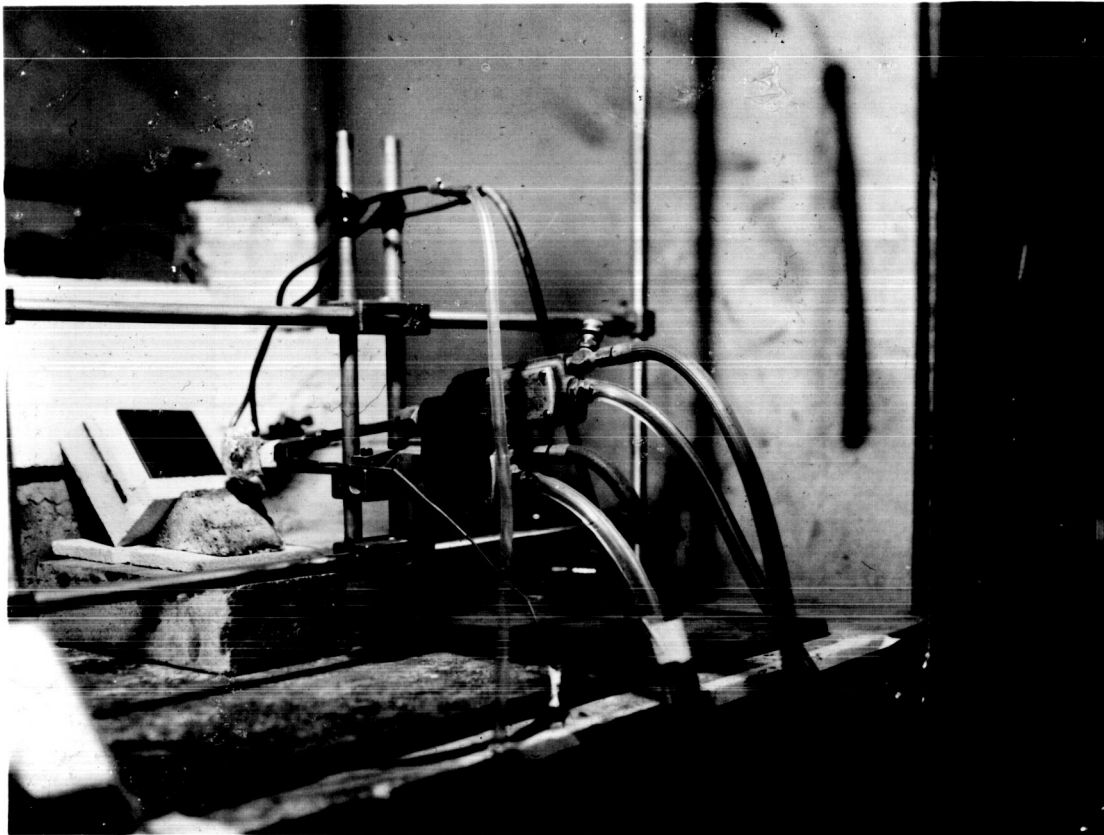


Figure 23

The two oxygen-hydrogen torches sued for high-temperature oxidation testing.

values are reported. The indicating pyrometer was useful in determining time to temperature, uniformity of temperature in the center of the specimen (a 1 1/2-inch diameter essentially uniform temperature zone), and any changes in temperature during the test.

The samples used for testing were 3 x 3 x 0.1 inch tungsten plates coated on only one side. Under single oxyhydrogen torch conditions, a 1/4-inch thick copper mask was placed over the edges of the plate to reduce edge oxidation. In the first dual torch test, this edge mask melted. Therefore, the edges of specimens tested with dual torches were exposed and oxidized badly.

5. Coating Systems and Evaluation

a. Tungsten Substrates

For the majority of normal ceramic coatings on metals, the thermal expansion is lower than that of the metal. Thus, as the system cools from the formation temperature to room temperature, the coating is placed in compression. However, the thermal expansion of tungsten is considerably lower than the refractory oxides in question, with the possible exception of partially stabilized hafnia. This means that as the systems are cooled, the coatings are placed in tension and develop a mosaic tensile crack pattern. Therefore, besides affecting the coating-substrate bonding, the thermal expansion mismatch has greatly dictated the type and complexity of the coating systems developed.

The tungsten particles in the coatings to be described were added to decrease the thermal expansion of the composite and to impart better thermal shock resistance through whatever mechanisms available, i.e., lower expansion and/or stress absorption.

The zirconia coating was never slated for a major oxidation protection role but was to serve as a research tool in the design of spray equipment and more advanced coating systems. Therefore, when the use of two tungsten-zirconia layers (43 w/o and 20 w/o tungsten) did not afford enough grading to alloy crack-free zirconia cover coats, the system was simplified so the total coating could be produced in one spraying.

Profile of a typical W-ZrO₂ system:

W substrate

3-5 mils of -74,+44 sprayed W undercoat

5-6 mils of 43 w/o W-ZrO₂

5-6 mils of ZrO₂

Such samples were used in developing the two hopper feed systems, the high-temperature oxidation test, the first sprayed tungsten undercoats, and many small but important points in spraying technique. Figure 24 shows a 3 x 3 inch tungsten plate coated with the above system after 300 seconds of exposure to a single oxyhydrogen torch; surface temperature was approximately 3750°F. The same test torch conditions caused surface regression of 30 mils/min for bare tungsten. Photomicrographs cut from the test plate in Figure 24 are shown in Figures 25 and 26. Figure 25 shows an area approximately 3/4 inch from the hottest point on the plate. Some of the W-ZrO₂ layer was converted to a yellow-green powder, removed during polishing, leaving the visible black streak which widens as it approaches the center of the hot zone. Figure 26 shows the center of the hot zone where the zirconia cover coat was removed during post-test examination. Here, nearly all the W-ZrO₂ layer was consumed; however, the sprayed tungsten layer is still present, indicating that the substrate was not consumed.

When retested, such coatings are blown apart along the horizontal and vertical crack patterns.

The coating development work with the partially stabilized hafnia indicated that the tensile cracking problem during coating formation was much less severe than for zirconia. Also, photomicrographs indicated a more dense structure was being obtained. After producing and testing various tungsten-zirconia-hafnia and tungsten-hafnia systems, the final design of two composite layers, a 40 w/o W-HfO₂ and a 10 w/o W-HfO₂ with a hafnia cover coat, seemed the most reliable. The hafnia cover coat of such a system did possess some microcracks but for the most part was sound and would not absorb writing ink. A photomicrograph of the typical structure listed below is shown in Figure 27.

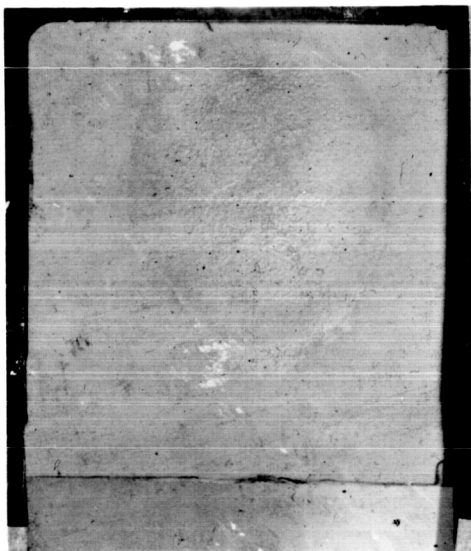
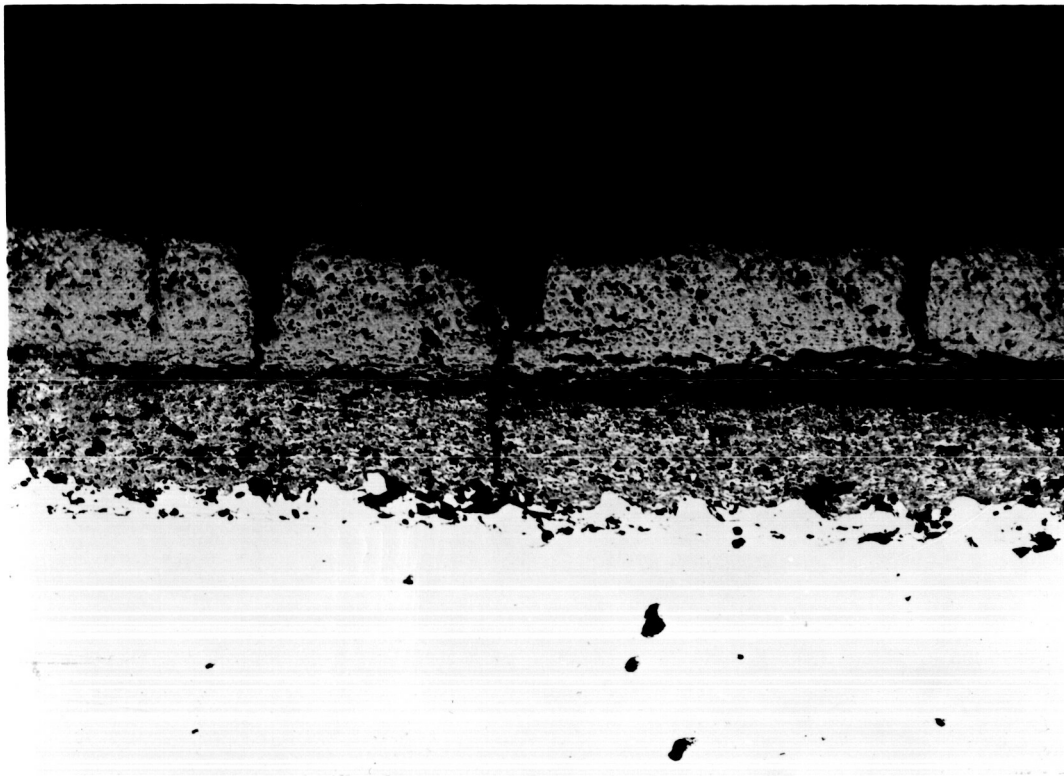


Figure 24

Tungsten coated with 3-5 mils sprayed tungsten, 5 mils of W-ZrO₂ grade, and a 5-mil ZrO₂ cover coat after oxidation test (one oxyhydrogen torch), 3750° F for 300 seconds.

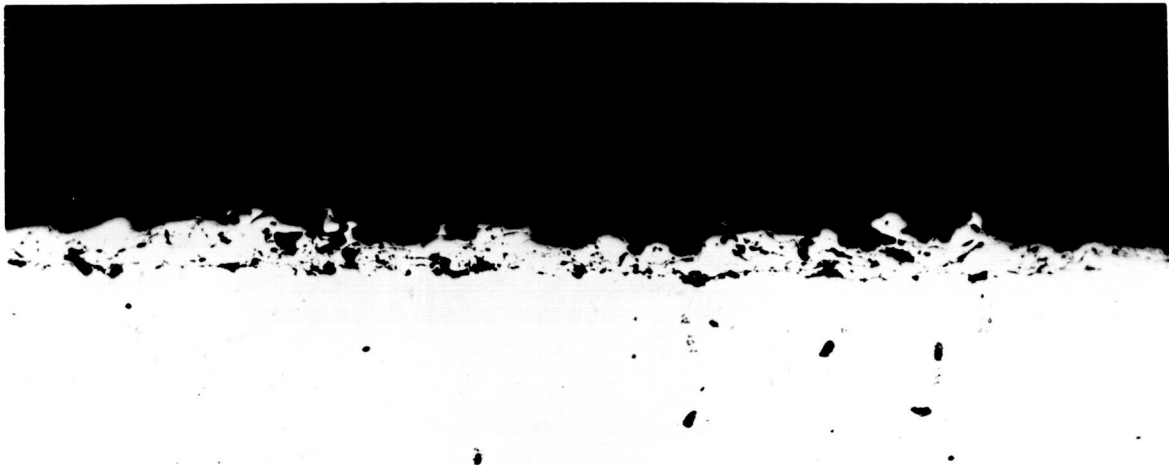


Neg. No. 24664

X100

Figure 25

Cross section through hot zone of plate shown in Figure 24. This section approximately 3/4 inch from hottest spot.



Neg. No. 24665

X100

Figure 26

Cross section through plate shown in Figure 24. Section from hottest spot. Cover coat and consumed grade layers have been removed.



_____ HfO₂

_____ 10 w/o W-HfO₂

_____ 40 w/o W-HfO₂

_____ Sprayed W

_____ W Substrate

Neg. No. 24660

X250

Figure 27
Typical Tungsten-Hafnia graded coating.

Profile of hafnia-tungsten system:

W substrate

3-4 mils of -74,+44 sprayed W undercoat

5 mils of 40 w/o W-60 w/o HfO_2

15 mils of 10 w/o W-90 w/o HfO_2 and HfO_2 cover coat*

Such a coating was tested under one oxyhydrogen torch for 600 seconds at $3600^\circ\text{-}3700^\circ\text{F}$ and cooled without any coating spalling. Upon retest, the coating was blown off in the hot zone within six seconds. The sprayed tungsten undercoat had become blackened, indicating some oxidation, but was still intact. The substrate was not consumed.

Two such plates were tested with the dual oxyhydrogen torch for 300 seconds at 4100°F . Both coatings protected the substrate during testing but cracked badly upon cooling.

As has been briefly mentioned, strontium zirconate was of interest because of its melting point of 5000°F and its reported ease of sintering to a dense structure. The literature indicates that the linear thermal expansion of the zirconate is close to that of fully stabilized zirconia; therefore some grading system had to be devised for the coating. Previous tests had shown that the 40 w/o W- HfO_2 composite fitted the tungsten substrate well, so the first strontium zirconate system evaluated was over the W- HfO_2 composite layer. The zirconate cover coat did have a mosaic crack structure but operated very well at $3600^\circ\text{-}3700^\circ\text{F}$ for 300 seconds.

The next coating modification was to add a low expansion phase to the zirconate; however, in this case hafnia was substituted for tungsten.

Profile of tungsten-hafnia-strontium zirconate:

W substrate

3-5 mils of -74,+44 sprayed W undercoat

3 mils of 40 w/o W-60 w/o HfO_2

This type of coating was tested for 420 seconds at $4000^\circ\text{-}4100^\circ\text{F}$ under the dual oxyhydrogen torch test. As with the other coatings, this system cracked during cooling. Figure 28 shows the plate after testing, and Figure 29 shows

* The two top layers were produced with the dual hopper system. The thickness represents a combined thickness. Timed spraying was utilized, and the top layer should represent approximately two-thirds of this total thickness.

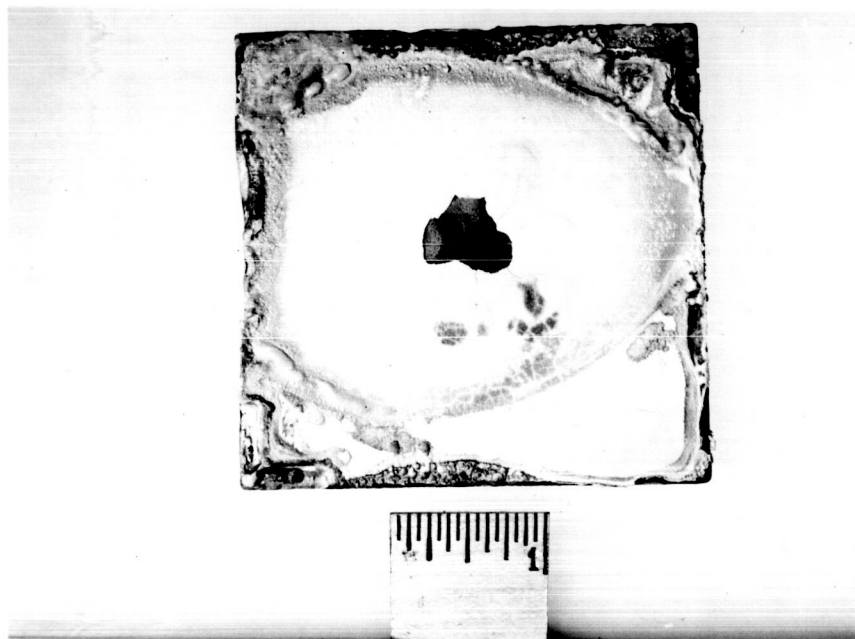


Figure 28

Tungsten coated with tungsten-hafnia-strontium zirconate composite (see text), after 420 seconds oxidation exposure at 4000° - 4100° F.



Neg. No. 24666

X100

Figure 29

Gross section of plate seen in Figure 28. View is from exposed area.

a cross section from the center of the plate and the very beginning of oxidation of the substrate itself.

A modification of the system just described was to add a hafnia cover coat, producing the system shown in Figure 30. Although no cracks are shown in this photomicrograph, the coating did contain some cracks, through the first two layers, to the tungsten-hafnia zone.

During the dual shock test this coating developed a blister, and the test was stopped after 120 seconds to determine the cause. The post-test examination indicated a localized interlayer failure. Since only one such coating was tested, it is not known if the lower expansion hafnia caused a stress buildup in the coating, or if this was just a defect induced by the coating procedure.

The last coating system evaluated on this program was the strontium zirconate graded with tungsten. A photomicrograph of this type of coating is shown in Figure 31.

Profile of strontium zirconate-tungsten system:

W substrate

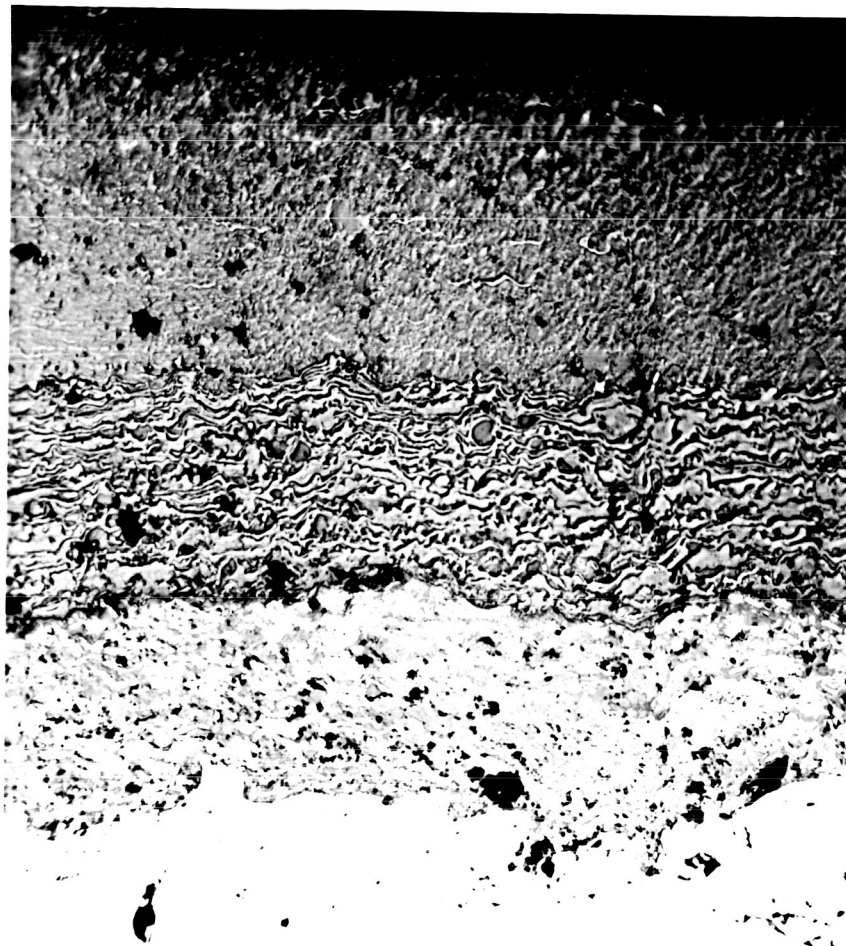
3-4 mils -74,+44 sprayed W undercoat

2-4 mils of 50 w/o W-50 w/o SrZrO_3

2-3 mils of 10 w/o W-90 w/o SrZrO_3

6-7 mils of SrZrO_3

Metallographic studies showed this system to contain some vertical cracks. Figure 32 shows a test plate after 300 seconds at 4000-4100°F. This sample drastically changed color from gray-pink to yellow-green in the hot zone. The mosaic crack structure of the original surface seemed to be covered with a glassy layer, and cracking upon cooling was not as severe as for other systems tested. Figure 33 is a cross section cut from the center of the plate seen in Figure 32.



_____ HfO_2

_____ 50w/o SrZrO_3 - 50w/o HfO_2

_____ 40w/o W - HfO_2

_____ Sprayed W

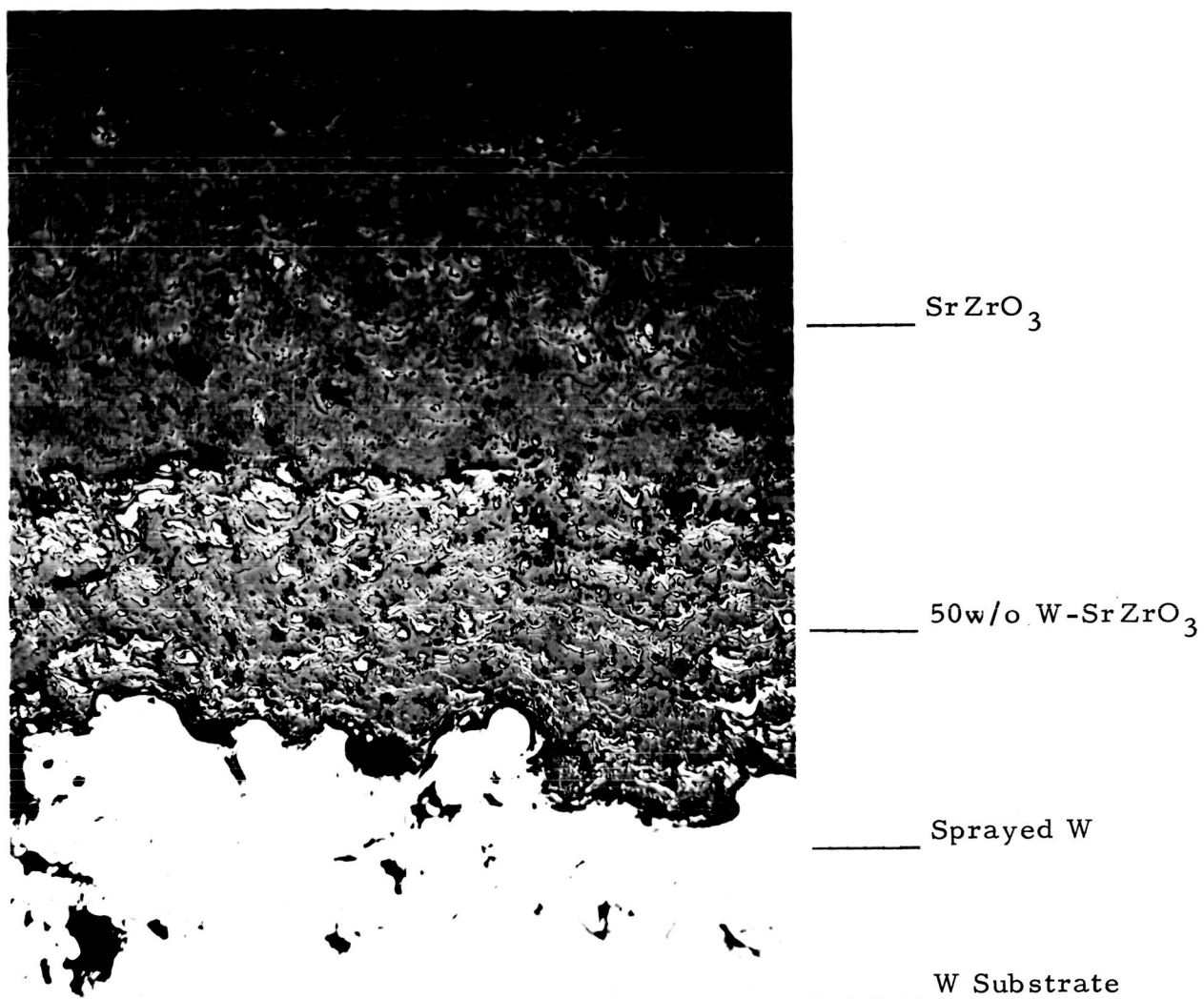
_____ W Substrate

Neg. No. 24462

X250

Figure 30

Tungsten-hafnia-strontium zirconate composite with hafnia cover coat.



Neg. No. 24661

X250

Figure 31

Tungsten-strontium zirconate graded coating.

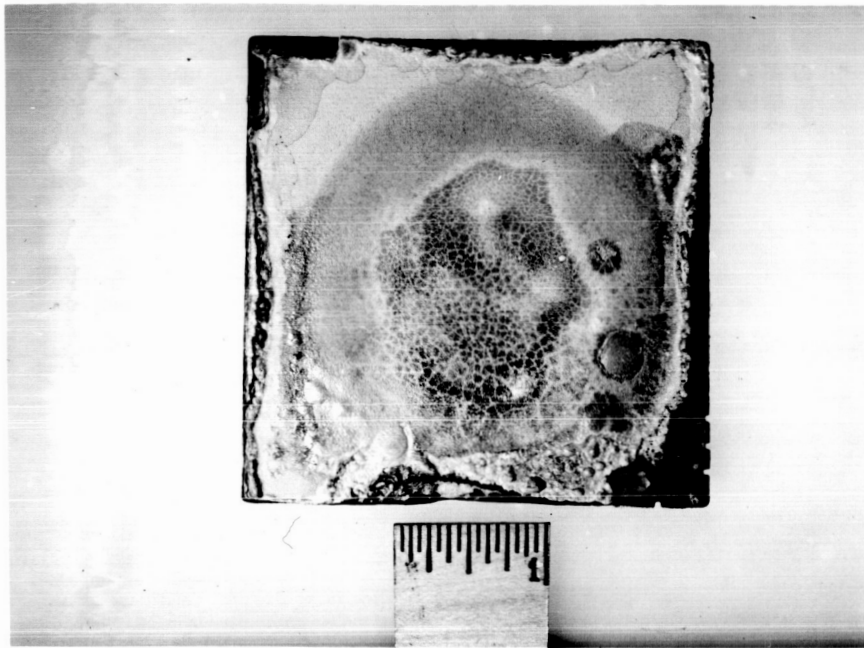
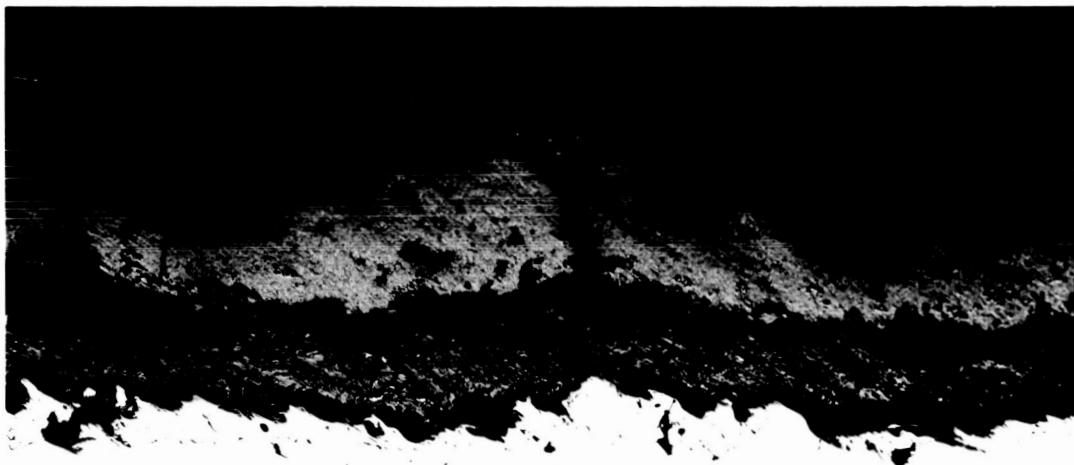


Figure 32

Tungsten-strontium zirconate coating after 300-second oxidation exposure at 4000°F.



Neg. No. 24663

X100

Figure 33

Cross section from center of plate shown in Figure 32.

b. Ta-10W Substrates

Limited work was conducted with Ta-10W as a substrate, but what was accomplished is significant.

The increase in thermal expansion of Ta-10W as compared to tungsten allowed crack-free hafnia coatings to be produced directly on Ta-10W, with substrate temperatures during coating as high as 1900°F. Figure 34 is a cross-section view of such a coating. The first hafnia coating to be tested was applied to a 3 x 3 x 0.1 inch Ta-10W plate which had an oxide film on it. This caused early coating-substrate bond failure and crack-free pieces as large as 4 inches in area spalled free. After this, the Ta-10W plates were soaked in a molten sodium hydroxide bath and sprayed with the tungsten undercoat prior to being coated with hafnia. Two coated plates were tested at 3600°-3700°F with one oxyhydrogen torch. The first hafnia coating was much too thin--3 mils in many areas. The second coating tested was much thicker.

Profile of hafnia coating on Ta-10W:

Ta-10W substrate

3-4 mils -74,+44 sprayed W undercoat

15 mils hafnia

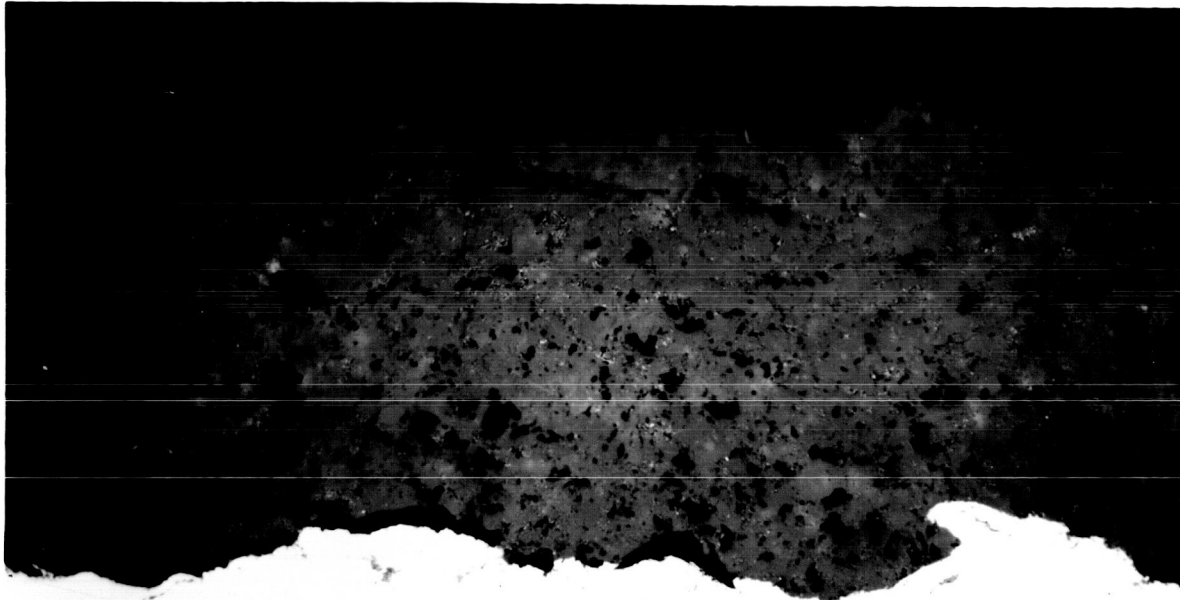
This coating operated at 3600°-3700°F for 150 seconds before a pinpoint spot developed in the hot zone. The test was terminated 30 seconds later when the spot grew into a hole exposing the substrate. During the 180 seconds of testing, the test plate actually deformed in the hot zone, becoming concave away from the test torch. The test plate after exposure can be seen in Figure 35. The portion of coating missing from the sample came off in one piece.

C. Other Graded and Reinforced Oxide Coatings

1. Introduction

The effectiveness of densely applied plasma-sprayed coatings in protecting tungsten from oxidation has been demonstrated in this program. It has also been well established that graded substrates of metal and oxide eliminate thermal shock failures on rapid heating. A separate effort was undertaken to apply graded oxide coatings by wet spraying or brushing of

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Neg. No. 24353

X500

Figure 34

Hafnia coating on Ta-10W substrate.

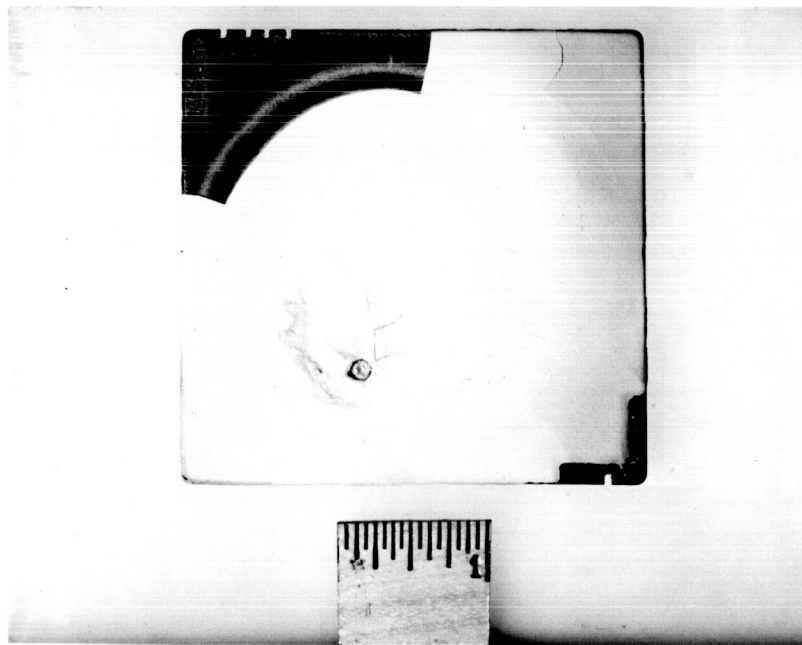


Figure 35

Hafnia (12-15 mils) on a Ta-10W after 180-second oxidation exposure at 3600° - 3700° F.

slurries with subsequent firing. This technique should prove much more convenient than plasma applications for coating of the internal surface of small-diameter rocket nozzles or similar structures.

Anticipated disadvantages of slurry applications are that much more shrinkage would be encountered on firing as compared to the "pre-shrunk" hot-sprayed material and the deterioration of substrate properties due to recrystallization during firing. Shrinkage must be minimized by optimization of particle size distribution, and recrystallization retarded by minimization of firing time and temperature, or by use of high tantalum alloys.

Advantages, in addition to the convenience of the cold slurry coating deposition technique, include more complete control of metal oxide gradation, layer thicknesses, and densification conditions. Much lower quantities of expensive refractory materials, such as hafnia, or materials requiring special handling, such as thoria, become airborne from the slurry.

A feasibility program was undertaken to demonstrate the value of the slurry technique as a means of applying protective oxide coatings to refractory metals.

2. Coatings Investigation.

a. General Considerations

The substrate investigated was exclusively tungsten during this feasibility investigation. Stabilized zirconia was selected as the outer coating material on the basis of availability and background experience on firing behavior. Although the plasma spray work and oxygen diffusion considerations indicate that stabilized hafnia would be a better ultimate choice, the investigation of shrinkage characteristics, densification as a function of firing time or by means of impregnation, gradation of thermal expansion, and means of substrate preparation for maximization of mechanical bonding could be more effectively conducted with the better characterized zirconia. Lime-stabilized zirconia was most convenient, being commercially available in various particle size grades, but it was felt that yttria-stabilized zirconia should also be investigated.

b. Equipment and Procedure

Two specimen configurations were employed. The bulk of the work was performed on 1/2 x 1 x 1/10 inch tungsten specimens. These were prepared by cleaning in hydrogen peroxide, sandblasted or coated with a plasma-sprayed tungsten deposit, as will be discussed later. The coating compositions in slurry form, using water as the vehicle, were sprayed on the plates by means of a Paasche AUTF air brush. Tungsten rods, 5/32 inch diameter and six inches long, were also coated generally by brushing after hydrogen peroxide cleaning.

The plate specimens were fired in an induction furnace with a graphite susceptor, utilizing an alumina firing tube with 2 inch internal diameter. Sample temperatures to 3180°F were readily obtained, but heating and cooling cycles were gradual to prevent thermal shocking the tube. All firings were in pure hydrogen atmospheres, with argon shrouding the susceptor.

Rod specimens were heated inductively within a quartz tube or by self-resistance, in vacuum, inert, or reducing atmospheres. Temperatures approaching 3600°F could be obtained by the induction apparatus, while the self-resistance unit could very quickly produce a central specimen zone temperature of up to the melting point of tungsten.

3. Materials Preparation

The lime-stabilized zirconia used in this program was a commercial -325 mesh material supplied by Zirconium Corporation of America. This was passed through a -325 mesh screen to eliminate some coarse material that was present. The broad spectrum particle size distribution of this product was considered as excellent for good packing. Graded mixes were made by simple admixture of tungsten powder.

Preliminary experiments with coprecipitated tungsten and zirconium oxides indicated that about an hour at 2200°F in hydrogen was sufficient for complete reduction to tungsten metal. This took the form of very fine particles blended with the refractory oxide particles. This procedure also fortuitously reduced a coarse, granular filter cake to a very fine powder. Based on this ability to obtain intimate mixtures, yttria-stabilized zirconia, with 12 weight per cent of stabilizer, was prepared

singly and with a 50 weight per cent tungsten admixture, using pure grades of zirconyl sulfate, yttria nitrate, and very water-soluble ammonium metatungstate. The plain oxide was fired in air at 2460°F. X-ray diffraction analysis showed it to be fully stabilized. The material with tungsten was fired in hydrogen at about 2010°F. Both materials were milled and screened with -325 mesh particles used in the preparation of coatings.

4. Coating Preparation and Evaluations

a. Tungsten Rod Specimens

The rod configuration presents a severe stress situation for coatings and has the opposite geometry of a rocket nozzle. However, the rod specimens could readily be coated, fired to very high temperatures, and examined while firing (through quartz tube or bell jar), and were most convenient for exploratory investigations of base coatings, thermal stability, and composite compatibility at elevated temperature.

Stabilized zirconia in water suspensions was painted onto the rods and fired at about 3600°F for various lengths of time, in vacuum and reducing atmospheres. The coatings were intact and crack-free if tungsten admixtures were employed, while oxide directly on the cleaned rods spalled. However, it was evident that superior adhesion was required for all cases. Tungsten-to-tungsten bonding requires very high temperatures so that even graded coatings require a mechanical bond mechanism.

Equal weight mixtures of tantalum carbide and tungsten powders, both -325 mesh, could be readily applied and obtained some adhesion to the rod on firing in vacuum at 3600° to 4500°F. The cohesive bonding, however, was poor, and the fired coatings were rather soft. It did appear that overcoats of zirconia could be applied and fired to good density. No deleterious interaction was observed between substrate, base coat, and top coat. The adhesion of zirconia to the carbide does not appear good enough to overcome thermal expansion stresses. Variations of the carbide-tungsten subcoat may be justified to improve sintering and bonding properties.

It was found that tantalum powder forms an excellent diffusion bond with tungsten at about 4000°F and higher, and may provide an excellent base coat for the mechanical bonding of an oxide coating. It was difficult to suspend the heavy refractory metal powder in a paint system for uniform

application on a rod. The grains could be well bonded with phosphotungstic acid solution (tungsten-to-phosphorus mol ratio of 12:1). A successful formulation was prepared by dissolving 20 parts of a high molecular weight polyethylene glycol (Union Carbide's Carbowax 4000) in 25 parts of Sylvania 251 phosphotungstic acid (38 per cent solids) and blending with 100 parts of a broad spectrum particle size tantalum powder (from Fansteel Metallurgical Corporation). The dissolved wax produced a high viscosity suspension which permitted a very uniform application of the metal. This paint was dried at 240°F to develop phosphate bonding. Upon firing by self-resistance in vacuum for 3 minutes, almost total diffusion with a smooth coating of tantalum on tungsten occurred in the central zone, which reached about 4500°F. Away from the hottest zone, where temperatures of 3600-4000°F were obtained, the powder was well sintered and quite uniform. Oxide cover coats could readily be applied over this area and good mechanical bonding could be anticipated. Future work would include overcoating and firing of graded refractory oxide layers on the sintered tantalum powder base.

Further work of oxide slurry coatings on rod specimens would continue in this exploratory line to rapidly evaluate substrate preparations and base coats and to investigate the thermal stability and compatibility of experimental composites. Major developmental efforts are better served with plate specimens because of the more favorable geometry.

b. Tungsten Plate Specimens

Coatings were applied to the relatively small 1 x 1 x 1/2 inch tungsten plates to investigate shrinkage characteristics, tendency to develop crack structures or to spall, behavior on refiring, acceptance of salt impregnations or additional layers and adherence. It is necessary to develop sufficient density for minimization of gaseous oxygen permeability and a graded expansion coefficient to maintain adherence during thermal cycling prior to evaluation of oxidation protection properties.

The prepared 12 per cent yttria-stabilized and the commercial 5 percent lime-stabilized zirconias, with 0-50 per cent tungsten admixture were applied by air brush to the prepared tungsten substrates. These were fired for 90 minutes or more at above 2910°F. With approximately 100 fired specimens, including refirings, nearly optimized procedures were developed

for good adherence, densification without excessive shrinkage or loss of bonding, and ability to thermal cycle.

Plasma-sprayed tungsten powder, of a 44-74 micron particle size range, provided an excellent base upon which the oxide coatings, without tungsten admixtures, were applied and fired. The first layer was thin; subsequent thicker layers can be applied and the piece refired, producing good densification with some tendency to a microcrack structure after several hours at 3090° - 3180° F. A thick initial oxide layer will shrink excessively and pull away from the substrate upon firing.

The use of the plasma-sprayed base was not considered appropriate for the purpose of this slurry application effort, which was to parallel the hot spray work. Surfaces grit-blasted with coarse silicon carbide could also be successfully coated with zirconia, fired, and refired with maintenance of adhesion, but adhesion was often inferior to that obtained on the sprayed tungsten. The tungsten base is difficult to grit blast, and a higher velocity jet or less friable grits may produce more undercutting of the surface with improved mechanical bonding. Diffusion-bonded tantalum powder, 200-325 mesh, provided an excellent base for the oxide coating and could be well penetrated. Microcracking occurs on densification, and the tantalum-tungsten bonding is lost if the diffusion zone is not adequate. A straight zirconia coating cannot maintain a bond on firing to a tungsten plate that has merely been cleaned.

In summary, the -325 mesh lime- or yttria-stabilized zirconia powders could be applied initially in a thin layer on a roughened tungsten substrate, fired at above 2910° F, followed by a thicker application of zirconia, and refired preferably above 3090° for more than 2 hours. Good densification is obtained without shrinkage failure other than incipient microcracking, and the coatings have undergone several refirings with further densification without loss of adhesion.

The prepared yttria-stabilized zirconia with 50 weight per cent of tungsten was applied to sprayed tungsten, grit-blasted, and hydrogen peroxide-clean substrates, and fired. The particles were soft and poorly bonded to each other and to the substrates. Yttria-stabilized zirconia top coats could then be applied and fired to good density without cracking or spalling.

However, the undercoating remained soft. Firing an initial application of base and top coat simultaneously resulted in loss of adhesion except when alternate layers of very thin applications were prepared. Alternating coatings of four thin layers each of the tungsten-zirconia and straight zirconia maintained good adherence on firing but were soft and porous. The multicoats performed more reliably on sprayed tungsten than on grit-blasted substrates.

When the quadruple, bilayer graded coatings were followed by a thick, straight oxide coating, the top coat could be fired to a very hard, dense, and much less permeable condition.

As the material with 50 per cent tungsten did not appear to lend itself to good bonding or densification, an equal weight mixture was made of the two prepared yttria-stabilized zirconia powders, with and without tungsten, to produce a material with 25 weight per cent tungsten. This produced much denser, less porous coatings on firing. The multicoat system with eight alternating layers of the new mixture and straight oxide, four layers of each, produced very adherent dense coatings on firing. This 25 per cent tungsten material was also very satisfactorily fired on grit-blasted surfaces.

Another multicoat graded coating, which could be applied to the grit-blasted tungsten and fired on one application, employed three layers of the commercial lime-stabilized zirconia admixed with 25, 10, and 0 weight per cent tungsten, going from bottom to top layer. A firing of about 90 minutes at 3090°F in hydrogen produced excellent densification and adherence.

Equal weight mixtures of tantalum carbide and tungsten, both -325 mesh materials, were applied to tungsten substrates as base coats. These were only weakly bonded on firing. Lime- and yttria-stabilized zirconia overcoatings were fired intact on this base with good adherence. It was thought that a dense oxide on a weakly bonded base may better withstand severe thermal stresses. Less microcracking occurred on oxide topcoats over this base than in the other composite systems.

Densification of the oxide coatings requires some shrinkage on sintering. To minimize shrinkage while achieving a lower permeability, attempts were made to impregnate the coatings which were initially fired, but still quite porous, with a solution of zirconyl nitrate prior to refiring.

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This technique has been successful in previous work in which flame-sprayed free-standing zirconia films were so impregnated and well densified on firing at 2730-2910°F. The attempts on this program were not very successful. There appeared to be little solution penetration, even on vacuum impregnation, and the coatings remained porous after repeated treatments. It may be necessary to modify the pore structure of the coatings to utilize this technique, perhaps through use of coarser grain zirconia powders.

The zirconyl nitrate must be fresh to be useful, as aged material, even in closed bottles, appeared much less soluble. Other zirconyl salts can be investigated, although previous experience indicated the greater usefulness of the nitrate.

5. Thermal Shock Tests

The development of the slurried oxide coatings has demonstrated that good adherence and refirability could be obtained with proper composite design. At this point, however, sufficient density has not been obtained to expect significant retardation of substrate oxidation at elevated temperature. Five specimens were prepared to determine the ability of some of the graded coating systems to withstand a severe thermal shock.

Four 1 1/2 x 1 1/2 x 1/10 inch tungsten specimens, blasted with silicon carbide grit, were coated as follows:

No. 18 (2 specimens): yttria-stabilized zirconia top coating over a base coat of an equal weight mixture of tantalum carbide and tungsten.

No. 31: 8 thin layers of yttria-stabilized zirconia, alternating 4 undercoats with 25 weight per cent tungsten with coatings containing no tungsten.

No. 34: 3 layers of lime-stabilized zirconia, with 25 weight per cent of tungsten in bottom layer, 10 per cent in middle layer, none in top layer.

These specimens were fired for about 2 1/2 hours above 2190°F, 1 3/4 hours of this time above 3080°F. The fired samples are shown in Figure 36. The thermal shock test consisted of exposing a specimen to an oxyhydrogen torch at a 2 inch distance using 60 cfh oxygen and 120 cfh hydrogen.

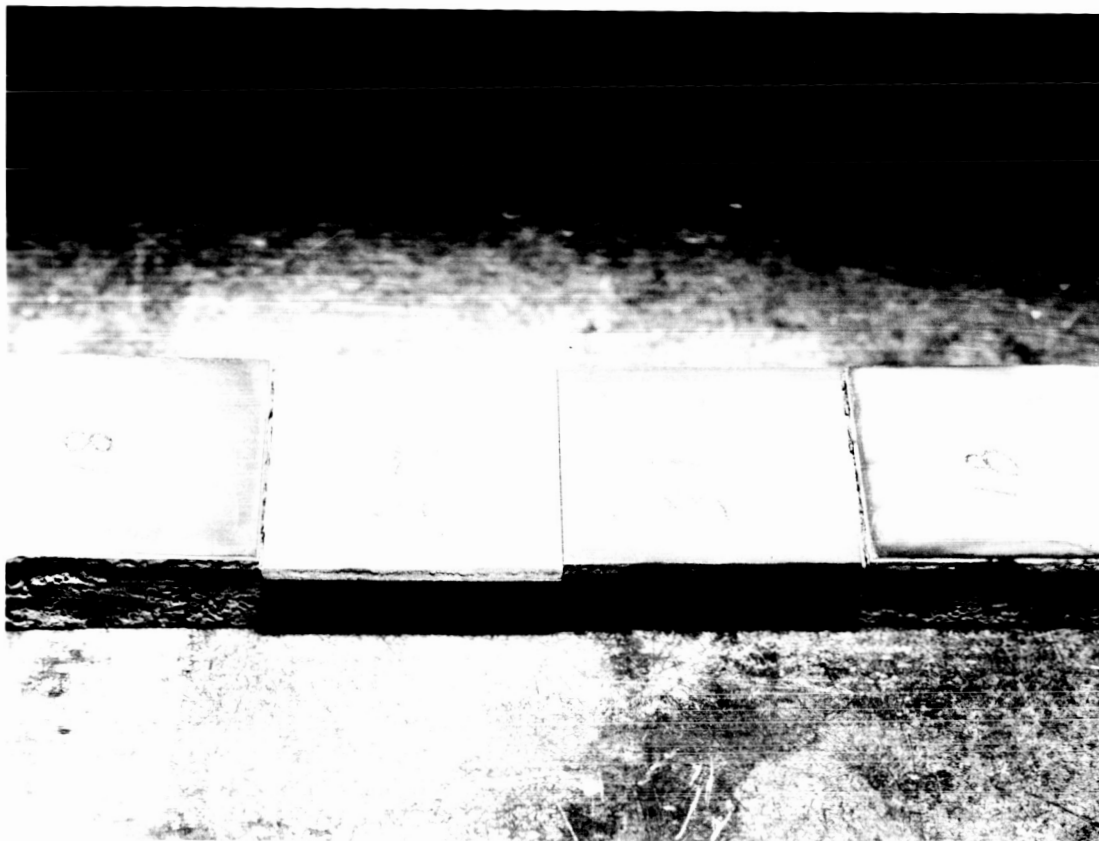


Figure 36
Fired composite slurry coated specimens prior to
thermal shock testing.

The first No. 18 specimen was heated for 5 seconds in which time the top coating was completely spalled off. The second No. 18 specimen also lost the top zirconia coating very quickly and after 13 seconds, in which time a hot zone temperature of about 3500°F was indicated on the Thermodot radiation pyrometer; the carbide coating blistered but was much toughened (see Figure 37).

Specimen No. 31 reached about 3600°F in 15 seconds and was exposed a total of 25 seconds. An extremely tough and adherent glass reaction product was produced, yellow-green in color. Although some fluxing and melting occurred, no thermal shock failure was observed (see Figure 38).

Specimen No. 34 also reached about 3600°F in 15 to 16 seconds and the torch cut off at 16 seconds. The coating was intact, yellow from tungsten oxidation, with no glass formation evident (see Figure 39).

It would appear that the graded and fired tungsten-zirconia composites are amply thermal shock-resistant and that further work should concentrate on reducing their oxygen permeability.

D. Metal-Modified Oxides

1. Introduction

The term metal-modified oxide has been generalized to encompass a wide range of metal-oxide composite structures. Historically, however, it is probably most appropriate to assign this name to the type of structure originally reported by Schwartz.⁽³³⁾ Thus, a metal-modified oxide structure is one in which the metallic phase is identical, or similar, to the metal constituent of the oxide. Structures of this type are generally produced by partially dissociating an oxide, in a manner similar to that described for nitrides previously in this report, or by preblending and sintering the metal-oxide mixture. The advantage of such a composite depends upon being able to disperse the metallic phase so that it provides enhanced shock resistance for the structure. Densification of the composites is accomplished by liquid phase sintering of the preblended constituents or by removal of oxygen from the oxide, causing precipitation of the metallic phase at grain boundaries. These methods were used to produce Ti-ZrO₂ and Zr-ZrO₂ bodies having remarkable resistance to thermal shock.⁽³⁴⁾

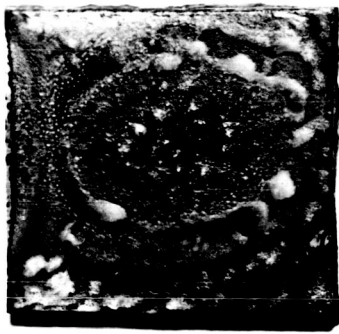


Figure 37

Thermal shock test on specimens with zirconia topcoat on TaC-W base coat tested for 25 seconds.

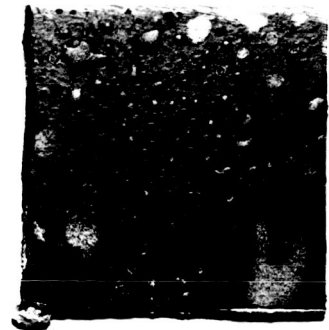


Figure 38

Thermal shock test on alternating zirconia layers with and without 25 w/o W. Tested for 5 and 13 seconds respectively.

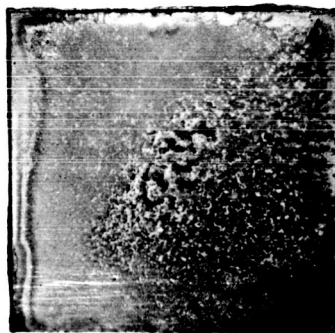


Figure 39

Thermal shock test on graded composite tungsten-zirconia coating. Tested for 16 seconds.

In applying this technique to the development of protective coating systems for tungsten, it was anticipated that excellent coating to substrate bonding could be obtained through alloying metallic constituents of the metal-modified oxide with the base metal. Initially the systems W-Ti-ZrO₂ and W-Zr-ZrO₂ were studied with the intention of extending his work to the systems W-Hf-HfO₂ and W-Th-ThO₂.

2. Experimental Procedure and Results

The only procedure that has been studied to date is that of pre-blending the metal-modified oxide constituents. Blends of -325 mesh ZrO₂, Zr, Ti, and TiH powders have been produced. The blends were suspended in HCl (0.5 cc/gm powder) and applied as slurries to tungsten rods by dipping. The following compositions were investigated:

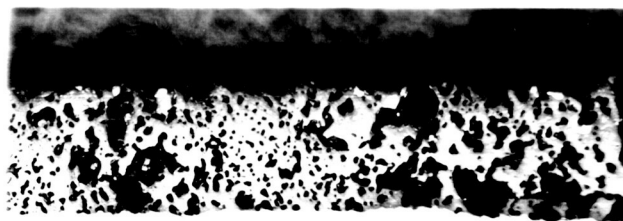
6.45 w/o TiH ₂	-	93.55 w/o ZrO ₂
6.45 w/o Ti	-	93.55 w/o ZrO ₂
10.0 w/o Ti	-	90.0 w/o ZrO ₂
15.0 w/o Ti	-	85.0 w/o ZrO ₂
7.62 w/o Zr	-	92.38 w/o ZrO ₂

The coated specimens were heated in vacuum, argon, and a 95 v/o argon-5 v/o hydrogen gas mixture to 3270°F under a variety of heating and cooling schedules. Heating in vacuum to 1000°F followed by slow heating in argon to 3270°F was found to be most satisfactory. The most adherent coatings were produced with the 6.45 w/o TiH₂ or Ti-containing mixtures. A photomicrograph showing this coating on a tungsten substrate produced under the conditions described appears in Figure 40. The metallic phase is randomly dispersed, and although the coating is somewhat porous, it is free of cracks produced due to thermal expansion mismatch. This coating also appears to have excellent resistance to thermal cycling. As yet, no specimens suitable for oxidation testing have been produced.

E. Metallic and Intermetallic Compound Coatings

1. Silicides

The use of siliconizing processes to protect tungsten from oxidation has been reported previously.⁽³⁵⁾ Coatings of this type have poor



Neg. No. 24400

X250

Figure 40

Ti-ZrO₂ structure produced on tungsten
by sintering in argon at 3270°F.

oxidation resistance in the temperature range 1200-2200°F due to "pest" formation and are limited in high-temperature protective capability due to formation of the W_{Si_2} - W_5Si_3 eutectic or through rapid formation of volatile SiO . The useful upper temperature limit appears to be 3400°F, depending upon external pressure, which is about the same useful limit encountered in glass-zircon coatings,⁽³⁶⁾ and the silicate coatings that have been developed for tungsten by Jefferys.⁽³⁷⁾ These coatings are not sufficiently refractory to be attractive for the purposes of this program. However, siliconized tungsten coatings were produced for use as a comparative standard in oxidation screening tests.

Silicide coatings were produced on tungsten by a pack cementation process and by slurry coating and diffusion using a mixture of silver and silicon powders. The pack coatings were made by embedding tungsten specimens in -325 mesh, solar cell grade silicon powder contained in a tantalum tray. This tray was placed inside an Inconel muffle along with a boat containing NaF as an activator. The muffle was evacuated, purged, and sealed. Thermal treatment of the tungsten was carried out for sixteen hours at 2200°F in this environment. After coating, the tungsten had a silicide layer which varied in thickness from 2 to 3.5 mils. The slurry coatings were produced by suspending -325 mesh silver and silicon powders in a collodion-acetone binder and painting this mixture onto tungsten specimens. The specimens were subsequently heat-treated in dry hydrogen at 2200°F for one hour. Coatings of both types have been tested in static air, an oxygen-acetylene flame, and an oxygen-hydrogen flame at temperatures in the range 2800-3400°F. Specimens tested in static air have lasted up to 7 hours at temperatures approaching 3400°F. Failure occurs in a region of the specimen which is subjected to lower temperatures during testing. Figures 41 and 42 show a coated tungsten rod that was resistance-heated at 2800°F for 7 hours. Failure occurred in a region of the specimen that was near the electrical contact blocks. Temperatures in this region were 2000 to 2200°F. The results of torch testing of siliconized tungsten are described in Section B-6a.

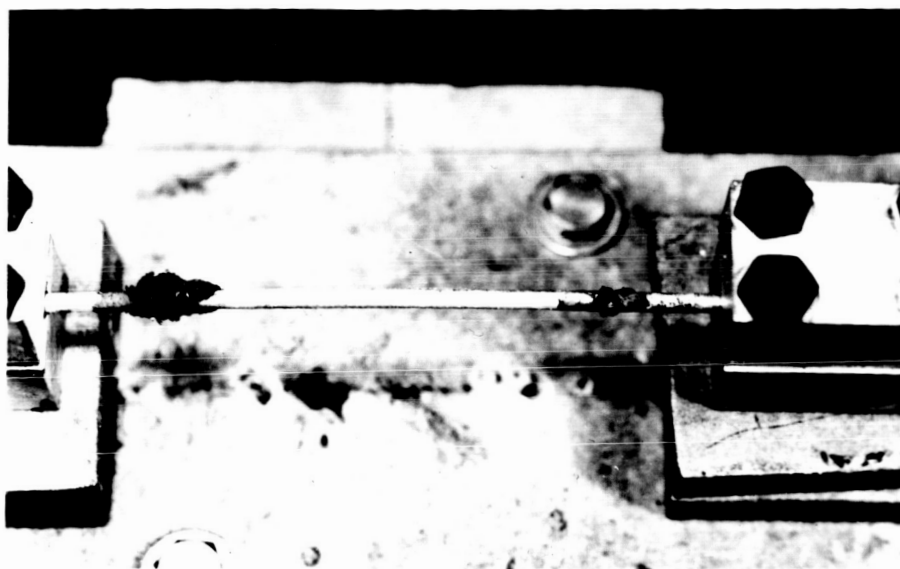


Figure 41

Tungsten coated with Ag-Si slurry after exposure in air for 7 hours at 2800°F.



Figure 42

Enlarged view of specimen shown in Fig. 41. The oxide growth is the result of "pest formation" in the region of the specimen which was heated to 2000°F - 2200°F during testing.

2. Composite Intermetallic Compound Coatings

The intermetallic compounds W_2Hf and W_2Zr , which melt at $4800^{\circ}F$ and $3950^{\circ}F$ ⁽³⁹⁾ respectively, were considered as forming the basis for high temperature protective coating systems for tungsten. The oxidation behavior of W-Hf alloys has been studied at low temperatures by Dickensen.⁽⁴⁰⁾ The results show that an alloy containing 32.5 w/o Hf, approximately W_2Hf , oxidizes at a linear rate at temperatures between 1830 and $2910^{\circ}F$. The rate of metal recession due to oxidation is, however, considerably lower than for unalloyed tungsten at these corresponding temperatures.

In view of the potential importance of this compound in forming the basis of a protective coating system for tungsten, several studies were carried out with the objective of determining its suitability.

The oxidation behavior of alloys based on W_2Hf has been studied at temperatures in the range 3600 - $4100^{\circ}F$. The alloys were prepared by arc melting 20-gram charges that were crushed and remelted a minimum of three times to insure homogeneity. Oxidation tests were performed by induction heating in air or by heating with an oxygen-acetylene torch. The specimen being tested was in contact with unstabilized ZrO_2 grain. Alloys in the system W-Hf-Y were studied. Of these, the compound $W_2Hf + 0.5$ w/o Y was found to be the most oxidation resistant. Oxidation exposure data for this compound and for pure tungsten appear in Table XII. The tests performed in static air indicate that the compound is reasonably oxidation resistant at these temperatures. However, during exposure in the torch tests considerably higher oxidation rates were observed. Further study of the oxidation behavior of these compounds is required before coating systems can be designed for rocket engine applications based on these compounds.

An alternate method of producing compounds based on alloys in the W-Hf and W-Zr systems was also investigated. This consisted of an attempt to develop coating systems containing these elements along with insoluble liquid metal carriers. The liquid metals were to provide a ductile substrate on which to form a HfO_2 or ZrO_2 scale while acting as a transfer medium for the oxidizable metal between the base coating and the scale. The coating, in effect, therefore would function similarly to the

TABLE XII
OXIDATION DATA FOR UNALLOYED TUNGSTEN
AND FOR W₂Hf-0.5 w/oY
HEATED IN AIR AND IN AN OXYGEN-ACETYLENE TORCH

Material	Method of Heating	Temp. , °F	Time, min.	Oxidation Rate Weight Change, mg/cm ² /min
Unalloyed W	induction	3800	10	-240
W ₂ Hf + 0.5Y	induction	3800	10	+2.1
W ₂ Hf + 0.5Y	induction	3500	12	-18.5
Unalloyed W	oxygen-acetylene torch	4100	10	-1020
W ₂ Hf + 0.5Y	oxygen-acetylene torch	4100	10	-118
W ₂ Hf + 0.5Y	oxygen-acetylene torch	3600	10	-65

tin-aluminide coating reported by Lawthers,⁽⁴¹⁾ or the Ag-Si coatings described in the previous section. To operate successfully, therefore, a liquid metal must be found capable of dissolving hafnium or zirconium but having a negligible or low solubility for tungsten. For this purpose, tin, silver, and copper were studied. In order to study the interactions produced between each of these carrier metals containing either hafnium or zirconium, two experimental procedures were employed. Mixtures of hafnium or zirconium powders with each of the carriers, in powder form, were placed into tungsten cups or were suspended in a binder and painted onto tungsten rods and subsequently interdiffused at temperatures between 1900-3300°F in vacuum or an inert gas atmosphere. In all cases, at high temperatures, extensive dissolution of the tungsten occurred and no compound layer was formed at the base metal interface. In some cases a compound layer could be formed at low temperatures, i.e. in the vicinity of 1900-2400°F. However, the compounds dissolved into the liquid metal upon heating to higher temperatures. An example of the compound layer produced with a Ag-Hf slurry fused on a tungsten specimen may be seen in Figure 43. It appears, based on these results, that a coating system of this type is not feasible with the combinations of elements that were studied.

IV. SUMMARY

The purpose of this program is to develop coating systems to protect refractory metals from oxidation when used in liquid fueled rocket engines at temperatures above 3600°F. For this purpose, oxidizable refractory compounds, graded metal-oxide and metal-bonded oxide structures, intermetallic compound and metallic coatings are being considered.

Of the oxidizable refractory inorganic compounds, that could be considered as suitable oxidation resistant coatings for tungsten and Ta-10W alloy above 3600°F, the nitrides and carbides of hafnium and zirconium were selected as offering the most promise. Experimental difficulties were encountered in trying to deposit hafnium carbide onto both of these materials due to a lack of thermal expansion matching and interface reactions that occurred during the plating process. Hafnium nitride coatings were deposited onto tungsten. The coatings were very adherent but contained radial cracks and as a result were not protective. Hafnium nitride coatings could not be



Neg. No. 24397

X250

Figure 43

Silver-hafnium slurry coating fused
onto tungsten at 2200°F for 1 hour.

applied to the Ta-10W alloy because of interaction of the alloy with the plating gas and with the nitride. Attempts to minimize this interaction by depositing a tungsten diffusion barrier on the alloy prior to nitride plating were only partially successful. The tungsten coatings contained voids or cracks which allowed interaction between the tantalum alloy and the nitride.

In order to eliminate the cracks that occurred in the hafnium nitride coating on tungsten, low pressure heat treatments were used to change the structure and composition of the nitride. Partial destabilization of the nitride in nitrogen at 5000°F produces a structure that appears to be free of continuous cracks. During oxidation at 4200°F, specimens treated in this manner are protected for at least 3 minutes by an adherent HfO_2 layer that forms on the surface. The life of such coatings under cyclic, rocket firing conditions will be studied.

A number of graded oxide coatings applied to tungsten by plasma spraying were evaluated. The grade layers were composed of tungsten and a refractory oxide applied by plasma spraying. The grade layers were applied over sprayed tungsten base coat which was found to be the most effective method for bonding the coating to the substrate. The oxides studied include CaO and Y_2O_3 - stabilized ZrO_2 , Y_2O_3 - stabilized HfO_2 and SrZrO_3 . Of these, the most refractory materials provided the greatest oxidation protection. Graded coatings of hafnia and strontium zirconate applied to tungsten by plasma spraying are protective for at least eight minutes at 4000°-4200°F. After oxidation exposure under these conditions the coatings lose their protective capability for further exposure. This loss may be attributed to coating shrinkage during testing that could result in failure by cracking during subsequent cooling or heating treatments, or to loss in adherence due to reactions in the grade layer. Thermal cycling of shorter duration may not produce coating failures. Further work will concentrate on improving the density of the oxide and improving the grading system. Interaction studies between tungsten and oxides will be made to help evaluate the cause of coating failure. These studies will include work on other more refractory oxides including ThO_2 .

An ability has been demonstrated for applying stabilized zirconia powders in water suspension to tungsten substrate to produce an adherent oxide coating. Although straight oxide coatings can be directly applied to a

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roughened surface, adherence is improved by using graded intermediate metal-ceramic layers to provide a gradual change in thermal expansion. This procedure is very convenient for the coating of the internal surfaces of rocket nozzles.

Firing temperatures of 3090° - 3180° F for a few hours were insufficient for full densification, but excellent thermal shock resistance was demonstrated with graded coatings. Oxidation protection properties were not evaluated due to the evident porosity.

A means for applying a uniform coating of tantalum powder on tungsten for diffusion bonding was developed. The resultant roughened surface appears useful for mechanical adhesion of the oxide coatings.

Graded coatings have been prepared by application of water suspensions of zirconia and tungsten powders and subsequent sintering with good adhesion to the tungsten substrate. Higher sintering temperatures will be required to obtain densification.

Metal-modified-oxide structures, produced by blending titanium or zirconium metal with ZrO_2 , have been applied to tungsten. These coatings are well bonded and free of continuous voids. Protective capability must be investigated. Impregnation of zirconia coatings with zirconyl salts should continue as an aid to densification. This may have to be investigated in conjunction with pore structure control.

Metallic coating systems were investigated in an attempt to find oxidation resistant materials which would be suitable as coatings. Alloys in the W-Hf-Y system appear to offer promise as potential coating materials for use at temperatures to at least 4200° F. More oxidation data will be required before coating development effort is initiated.

The oxidation behavior of siliconized tungsten was studied and coated samples of this type were used as control standard for torch test evaluations. The protective capability of these materials was found to be similar to that reported by other investigators.

Composite metallic and intermetallic compound coatings, of the tin-aluminide type, based on the systems Sn, Ag, and Cu with Hf and Zr were investigated. In all of these systems there is either insufficient diffusional stability or extensive solubility of the base metal at elevated temperatures.

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In view of the objective of establishing the state of technology in this area, it appears that the most rapid progress could be made in the area of graded oxide coatings on tungsten. Although the other methods that have been investigated offer some promise, the immediate objectives of this program can be attained more directly by concentrating on the refractory metal-oxide coating systems. Future work will be primarily in this area.

V. CONTRIBUTING PERSONNEL AND LOGBOOKS

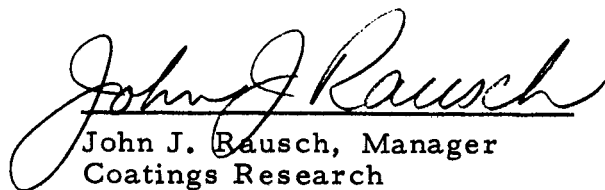
The following personnel have contributed to the work reported herein:


J. L. Bliton	- Associate Ceramic Engineer, Plasma Spray Coatings
M. Braitberg	- Technician
T. Caskey	- Technician
F. Hirsch	- Technician
L. I. Kane	- Assistant Metallurgist
D. Lofton	- Technician
J. Miller	- Assoc. Electrochemist
F. Onesto	- Technician
J. J. Rausch	- Project Leader
H. L. Rechter	- Project Engineer
D. C. Schell	- Ceramic Engineer
J. Stuart	- Assistant Scientist

Data for this program are recorded in IITRI Logbooks:

C 12347	C 12695	C 13087
D 1330	C 12698	C 13089
C 12677	C 13076	C 13093
C 12682	C 13080	C 13097
C 12689	C 13081	C 12791
C 12691	C 12604	C 12436
C 12796	C 13162	C 13299

Respectfully submitted,
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John J. Rausch, Manager
Coatings Research


R. J. VanThyne,
Assistant Director
Materials and Structures Research

JJR:cbm

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